Pedagogic notes on Thomas-Fermi theory (and on some improvements): atoms, stars, and the stability of bulk matter

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In the more than half century since the semiclassical Thomas-Fermi theory of the atom was introduced, there have been literally thousands of publications based on that theory; they encompass a broad range of atomic bound-state and scattering problems. (The theory has also been applied to nuclear physics and solid-state problems.) We will concentrate here on the essence of the theory, namely, its implementation of the uncertainty and exclusion principles and of the Coulomb or Newton force law. Since we are often far more interested in physical concepts than in numerical accuracy or rigor, we will sometimes consider the implementation in a qualitative rather than quantitative fashion. The theory is then capable of giving only qualitative information about a system—one obtains the dependence of the total ground-state binding energy E and radius R of an atom on the nuclear charge Z, for example, but one obtains only rough estimates of the numerical coefficients; in compensation, the calculations are often literally trivial, very much simpler than the already simple Thomas-Fermi calculations. A point to be emphasized is that in the course of obtaining an estimate of E and R of an atom in a Thomas-Fermi approach, one also obtains an estimate of the electronic density, and, particularly if the analysis is more than simply qualitative, an electronic-density estimate can be very useful in a wide variety of problems. We include a short comment on alternative formulations of Thomas-Fermi theory in a D-dimensional space. We will review the applications of the theory, from both qualitative and (Thomas-Fermi) quantitative viewpoints, to heavy atoms, where we are concerned with a Coulomb interaction, and to neutron stars and white dwarfs, where we are concerned with a gravitational interaction and with gravitational-plus-Coulomb interactions, respectively. In the latter case, the first two Coulomb corrections are evaluated. Very rough (relativistic) estimates are made of the conditions under which heavy atoms, neutron stars, and white dwarfs collapse. A one-dimensional Thomas-Fermi-like theory also exists for heavy atoms in a uniform strong magnetic field B, of the order of the field believed to exist at the surface of a neutron star. Here, too, the qualitative picture immediately gives some of the main results, namely, the dependence of E and R on B and Z. We also comment briefly on some relatively recent and very recent developments in Thomas-Fermi theory. These include a proof of the stability of matter. Though it was first proved by Dyson and Lenard, we consider the Lieb-Thirring proof, both because it is much simpler and because it makes extensive use of Thomas-Fermi theory, including a no-molecular-binding theorem that follows in the Thomas-Fermi approximation: Teller proved that, in that approximation, atoms could not form molecular bound states. These developments also include (a) the Lieb-Simon proof that the prediction of the theory that $E=-c_7Z^{7/3}$, with c_7 a specified coefficient, becomes *exact* at $Z\sim\infty$, (b) the Scott-$c_6Z^{6/3}$ correction term, with c_6 specified and now known also to be *exact*, and (c) the Schwinger estimate of the coefficient c_5 of the $Z^{5/3}$ term, which there is good reason to believe is exact. The many digressions include comments on QED, on lower bounds on the ground-state energy of a system, and on mini-boson stars.

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I. INTRODUCTION

A beautiful and correct theory can be disfigured by an approximation introduced to simplify a calculation, but there are also approximations that retain the elegance of the correct theory and provide new and deep physical insights. An *extraordinarily* simple approximation to the Schrödinger theory of a many-electron atom, one that is extremely useful in providing quick numerical estimates and a physical feel for many problems, is the model published independently by L. H. Thomas (1927) and E. Fermi (1927). [I am not aware of any remarks by Fermi as to the extent of the effort he put into the development of the theory, but, as one indication of the simplicity of the theory, it is interesting to record that Thomas has stated that he spent no time at all on the development of the model (and did it to get practice in the numerical solution of differential equations).] The model is normally known in the United States, where Thomas has long resided, and surely in Wales, where he was born, as the Thomas-Fermi (TF) model, but in Italy it is also known as the Fermi-Thomas model. (Lieb has commented that he prefers the order Thomas Fermi since it then sounds like the name of a person.)

It is of course impossible to patent an idea. If it were, it would be interesting to contemplate how profitable it might have been for Thomas and Fermi, following their independent publications in 1927, to have formed a Thomas-Fermi Model Company. It would certainly have been a growth industry, for there have been literally thousands of published articles based on the model. (An all-encompassing review is therefore precluded.) As will be clear from the discussion, many very distinguished physicists have played a role in the further development of the theory; the model is so well known that the original papers are almost never referred to. The longer reviews include a book by Gombás (1949), articles by Lieb and Simon (1977) and by Lieb (1976, 1981), and long sections of books by March (1975) and Thirring (1983). March's book, incidentally, contains the original paper by Thomas and an English translation of the original paper by Fermi. Most quantum mechanics texts devote at least one or two sections to the model. The model has been heavily used by atomic physicists in studying fundamental questions and in applications, including areas of astrophysics and plasma physics. [There have also been many applications in condensed-matter physics, and the model has been used a fair number of times in nuclear physics; Serber (1976) is one example. To my knowledge the model has not been a popular item among axiomatic field theorists.] We note that the model is a universal one—since the TF potential for a neutral atom scales, one calculation provides the charge distribution for a neutral atom of any nuclear charge Ze in its ground state; the model can therefore immediately be used, in the Born approximation, for a wide range of elastic-scattering problems. The model has also been used to provide numerical estimates for an enormous range of bound-state properties. [Since TF calculations are relatively simple, they are often used to scale results. One starts with a more reliable value than that estimated by TF theory itself of, for example, the elastic differential cross section at θ_0, $\sigma(\theta_0)$, provided by experiment or by a more complete calculation. One then uses TF theory to estimate $\sigma(\theta)$ for all θ, obtaining the angular distribution from TF theory and the normalization constant from the value of $\sigma(\theta_0)$ obtained elsewhere.] The TF model also has been used to study exotic questions such as the value of Z for which an orbital angular momentum quantum number l of an individual electron, an f or a g state, for example, first appears (Fermi, 1928); see, also, Rau *et al.* (1972), and references therein.

With the passage of time, the nature of its use has shifted somewhat. It is still very useful for making numerical estimates, as, for example, in the use of model potentials based partially on the TF potential, but with the advent of high-speed computers simple TF estimates are often preliminary ones, to be supplemented by, for example, Hartree-Fock or variational-principle calculations. Relatively recently, an ingenious positive use (Lieb and Thirring, 1975) of the main *failure* of the TF model, its inability to allow atoms to combine to form a molecule (Teller, 1962), provided by far the simplest proof of the "stability of matter," that is, a proof that the nonrelativistic binding energy of a system of electrons and nuclei is bounded from below by a negative multiple of the number of particles. [That matter is stable was first proved by Dyson and Lenard (Dyson, 1967; Dyson and Lenard, 1967; Lenard and Dyson, 1968; see, also, Dyson, 1968).] It is an astonishing fact that a theory developed to study a *single* atom with $Z \sim \infty$ can be used to study the interaction of an arbitrarily *large number* of atoms with, for example, $Z=1$! Very recently it was realized (Martin, 1988a, 1988b) that a knowledge of the nonrelativistic energies of a system can lead to an upper limit on the coupling constant if the (model) relativistic system is to have an energy bounded from below.

It is important to try to understand why the TF model has been so useful in so many different ways. The most obvious reason is that it provides an *exact* result for the energy of an atom in the limit $Z \sim \infty$. [This has been "known" to physicists since the TF model was first introduced, but it was proved only recently (Lieb and Simon, 1977).] A second reason is its universality, noted above. Perhaps the best reason is that, for many problems, it incorporates in the simplest possible form so much of the essential physics, namely,

(i) the uncertainty principle,
(ii) the Pauli exclusion principle,
(iii) the Coulomb force law.

(As we shall see, and as is hardly surprising, it works just as well for the gravitational case; it can therefore be used to study neutron stars and white dwarfs as well as normal atoms.) Many of the discussions in the present article are watered-down versions of TF theory, encompassing (i), (ii), and (iii) in a more rudimentary fashion than does TF theory.

It is interesting to observe (Lieb and Simon, 1977) that, whereas a standard simplifying approximation is the replacement of a nonlinear equation by a linear equation, the TF model is obtained by proceeding in the opposite direction, with the approximation of the linear Schrödinger equation by the nonlinear TF equation, which involves the number density $n(\mathbf{r})$. The TF equation is nevertheless an enormously simplifying approximation, with the object to be determined simply $n(\mathbf{r})$, rather than the wave function, which depends upon the coordinates of each of the electrons.

Section III consists of preliminary material, much of which many readers will wish to omit, but the material on the Sobolev inequality, which, for the particular case considered (and probably for a number of other cases), gives a more useful (lower) bound on the kinetic energy of a particle than is obtained directly from the uncertainty principle, and on an extension of the virial theorem, which gives *two* relations among components of the total energy, may be unfamiliar. In Sec. IV we develop the TF formalism, progressing from a qualitative picture that is even simpler than the TF theory but gives about the same results. In Sec. V we give some results in TF theory, for real and model atoms. In Sec. VI we apply TF theory to neutron stars and to white dwarfs, at the qualitative and semiquantitative level, while in Sec. VII we do the same for a TF-like theory of atoms in an intense magnetic field, such as that at the surface of a neutron star. Thomas-Fermi theory gives a ground-state energy $E=-c_7 Z^{7/3}$ Rydbergs, with c_7 a known constant, for a neutral laboratory atom. Section VIII begins with some comments on the no-molecular-binding theorem of Teller, which shows that TF theory is such a *poor* theory, with respect to molecular applications, that it does not allow for the formation of molecules from atoms. It then gives a brief discussion of developments in the study of the stability of matter, a subject of general conceptual interest, and one which, in the author's opinion, has lent itself to some of the most beautiful work in mathematical physics of the last 25 years; that opinion is shared by a number of committees that award prizes. That matter is stable was, as noted above, first shown by Dyson and Lenard (Dyson, 1967; Dyson and Lenard, 1967; Lenard and Dyson, 1968) in a stunning *tour de force.* The exquisite proof of Lieb and Thirring (1975) is of greater interest to us, for, capitalizing on a major *defect* of TF theory, they base their proof on the no-molecular-binding theorem which arises in a TF context. [Dyson (1967) also showed that the fermion property of electrons was not only a sufficient but a necessary condition for the stability of matter; matter would be unstable, that is, the energy would increase faster than the number of electrons, and matter would therefore have no extensive properties, if electrons were bosons.] In Sec. IX we discuss the leading correction to TF theory, associated with the strongly bound inner electrons, the Scott Z^2 term, first suggested by Scott (1952), and contributions to the analysis of this term by Ballinger and March (1955), by Lieb (1976), and, most recently, by Schwinger (1980). Section X gives the analytic evaluation of the coefficient of the $Z^{5/3}$ term by Schwinger (1981), which contains an exchange-term contribution (Dirac, 1930), and a quantum kinetic-energy correction associated with the bulk of the electrons. Section XI contains a number of notes.

Many of the sections can be read independently. In particular, much of the later material can be read independent of the material in Secs. IV and V on atoms under the usual laboratory conditions.

Remarks on the foundation of the theory

The need for a review of some of the recent developments in TF theory may be clear, but a comment on the need to discuss the foundation of a theory now some 60 years old, as we do in Sec. III and part of Sec. IV, may be in order. We include this material not for completeness but because most of the treatments in the literature emphasize the applications rather than the foundations, and some are very misleading in their treatment of the foundations; the logic used is faulty, and the fact that the result obtained is correct for the case of the neutral atom—often the only case treated, although, to be sure, the most important case—is largely accidental. (It is astonishing but true that very few textbooks give the TF differential equation in its correct form!) We shall consider the problem in some detail in Secs. IV and V, but the essential points are easily made. First, in using the calculus of variations to obtain the TF differential equation, one often treats the number density $n(\mathbf{r})$ as if it allowed an arbitrary variation; in fact, there are regions where $n(\mathbf{r})=0$, and there one must have $\delta n(\mathbf{r})\geq 0$. We shall return to this matter later. The second point is the following. Let $p_F(\mathbf{r})$ be the Fermi momentum at $\mathbf{r}$, that is, the upper range of the momentum distribution demanded by the Pauli principle and determined by the local electron density, and let $\epsilon_F(\mathbf{r})$ be the associated Fermi energy. Further, let $V(\mathbf{r})$ be the effective potential energy at $\mathbf{r}$. It is then often stated that

$$\epsilon_F(\mathbf{r})\equiv p_F^2(\mathbf{r})/2m+V(\mathbf{r})=0\ , \tag{1.1}$$

that is, it is often assumed that the maximum energy $\epsilon_F(\mathbf{r})$ of an individual electron at $\mathbf{r}$ must be zero in order to prevent the electron from escaping to infinity. But escape is prevented if

$$\epsilon_F(\mathbf{r})\leq 0\ ; \tag{1.2}$$

there is no physical argument that requires the electrons at $\mathbf{r}$ to pile up until $p_F^2(\mathbf{r})/(2m)$ is *equal* (and opposite) to $V(\mathbf{r})$. To see that the assumption that $\epsilon_F(\mathbf{r})$ must be equal to zero can be wrong, consider a positive ion, with a nuclear charge Ze and $N(<Z)$ electrons. Assuming spherical symmetry, the shielding of the nucleus by the electrons will be incomplete in certain regions, and we have, for all r,

$$V(r)\leq -(Z-N)e^2/r\ , \tag{1.3}$$

with the inequality approaching an equality as $r\sim\infty$. If Eq. (1.1) were correct for positive ions, we would have, for all r,

$$p_F(r)\geq [2m(Z-N)e^2]^{1/2}/r^{1/2}\equiv K/r^{1/2}\ .$$

Now an essential underpinning of TF theory is statistical quantum theory [which incorporates items (i) and (ii) above]; for the temperature $T=0$, the number of electrons allowed in a volume of phase space $d\mathbf{r}\,d\mathbf{p}$ is then equal to $2\,d\mathbf{r}\,d\mathbf{p}/h^3$, the factor of 2 originating in the spin of the electron. If then N' is the number of electrons that can be supported by $V(r)$, we have

$$N'=(2/h^3)\int\int d\mathbf{r}\,d\mathbf{p}$$
$$=(2/h^3)(4\pi)^2\int r^2\,dr\,p_F^3(r)/3\ .$$

If Eq. (1.1) and the inequality for $p_F(r)$ to which it leads were correct for positive ions, we would find

$$N'\geq(32\pi^2/3h^3)K^3\int_0^\infty r^{1/2}dr=\infty\ ;$$

Eq. (1.1) is simply not valid for positive ions.

We assumed just above that T was zero, or, more precisely, that kT is negligible with respect to the Fermi energy. That would of course not be true (to cite one counterexample) for the Sun.

[Note that the potential in TF theory is that seen by a test particle of infinitesimal charge. Thus *all* of the electrons, including the one whose potential energy is to be determined, contribute to the potential. It is for that reason that we took the coefficient in Eq. (1.3) to be $Z-N$ rather than $Z-(N-1)$. When we consider negative ions in TF theory, the effective potential at large r, where the outermost electron will tend to be, will be dominated by a repulsive Coulomb component, even for only one additional electron, that is, even for $N=Z+1$. In a real atom, on the other hand, for a negative ion with $N=Z+1$ the potential seen by the outermost electron will be zero in a first approximation, and small corrections, such as the attractive polarization potentials induced by the outermost electron, may be strong enough to bind the extra electron. That can scarcely be expected to happen in TF theory, and, indeed, one of the failures of TF theory is that it cannot account for any negative ion. Without giving any details, we note that a simple modification of TF theory can account for the fact that there are negative ions with $N=Z+1$ but none with $N>Z+1$ (Benguria and Lieb, 1985).]

Not only can we have $p_F^2(\mathbf{r})/2m$ less than rather than equal to $-V(\mathbf{r})$, but in TF theory we can have $p_F(\mathbf{r})=0$, and therefore $n(\mathbf{r})=0$, over three-dimensional regions where $V(\mathbf{r})$ is nonvanishing (and negative). This situation is quite different from that which exists for the true atom, described by a (linear) Schrödinger equation. Consider a spinless particle with a wave function $\Psi(\mathbf{r})$. Apart from regions where the potential is infinitely positive, $n(\mathbf{r})=\int|\Psi(\mathbf{r})|^2d\mathbf{r}$ and therefore $\Psi(\mathbf{r})$ cannot vanish over a three-dimensional region, for then $\Psi(\mathbf{r})$ and its derivatives would vanish and the only solution of the Schrödinger equation would be the trivial solution $\Psi(\mathbf{r})=0$ everywhere. For a many-electron system, the Schrödinger wave function Ψ is a function of all of the spatial and spin coordinates, but $n(\mathbf{r})$, obtained from $|\Psi|^2$ by summing over spins and integrating over all but one spatial coordinate, remains a function of just one coordinate, $\mathbf{r}$, and it is again true that $n(\mathbf{r})$ cannot vanish over a three-dimensional region lest Ψ vanish everywhere. As noted above and as will be discussed later, one important consequence of the fact that $n(\mathbf{r})$ in TF theory can vanish over a three-dimensional region is that the ground-state energy of a positive ion in TF theory will *not* be stationary with respect to small variations of the number density about the number density for the ground state.

There are a number of excellent treatments of the applications of TF theory, and there are of course some good treatments of the foundations of the theory, including some listed above and Bethe and Jackiw (1986). An extremely careful and thorough treatment of the foundations of TF theory is given in Lieb and Simon (1977), which also contains a wealth of new theorems, but this article was written for a mathematical journal and will have its strongest appeal for the mathematically oriented reader; an experimental physicist poorly trained in mathematics will not find it bedtime reading. Parts of Sec. III represent watered-down versions of a brief portion of the Lieb-Simon article, which may well remain, with the section of the book by Thirring (1983) and reviews by Lieb (1976, 1981), the most complete treatments of the subject for some time to come. (Lieb's 1981 review not only contains a number of new results in TF theory, but also presents a rather thorough mathematical treatment of TF theory as modified by Dirac to include exchange and as modified by von Weizsäcker to include kinetic-energy corrections originating in the variation in the electron number density.) One of the objectives of the present unsophisticated review is to interest some readers enough to get them to study these treatments. Unless there is some compelling reason to include them, "mathematical" questions are largely ignored in our treatment. (The tastes and abilities or lack thereof of the author make this almost necessary.) Thus, in obtaining the TF differential equation for the electron number density $n(\mathbf{r})$ from the Lenz energy functional $\mathbf{E}[n]$, it will be *assumed* that there is an $n(\mathbf{r})$ that minimizes $\tilde{E}[n]$. Theorems obtained under such assumptions and yet widely held in the physics community are referred to by Lieb and Simon (1977) as "folk theorems."

We close Sec. I with a remark that may make TF theory more appealing to "practical" readers. It is certainly true, as stressed by Lieb, that as an atomic theory which becomes exact as the number of electrons $\sim\infty$ (the only other exact atomic theory being that for one-electron systems), TF theory warrants careful study. But since it is almost certain (and will henceforth be assumed) that corrections to the theory are of the order of 25% even for Z as large as 64, the pragmatic reader might well ask: "What can the theory do for me?" In response, we note first that the two leading corrections, of relative order $Z^{-1/3}$ and $Z^{-2/3}$, have been obtained (Scott, 1952; Ballinger and March, 1955; Lieb, 1976, 1981; Schwinger, 1980, 1981); the $Z^{-1/3}$ correction is known to be exact and the $Z^{-2/3}$ correction is believed to be exact. Further, it has been observed in the past that the corrected theory works much better for small Z than might be expected of a theory with corrections that seem to fall off as powers of $Z^{-1/3}$; indeed, at least for some very simple models, Shakeshaft and Spruch (1981) showed that $E_{\text{smth}}(Z)$, the smooth and dominant part of the energy of an atom as a function of Z—we shall be more precise in Sec. XI.C—has an expansion in powers of $Z^{-1/3}$ that converges for $Z>(18\times 3^{1/2})^{-1}=0.0323$, an expansion that converges *rapidly* even for Z equal to unity! We can therefore hope that corrected TF theory will be reasonably accurate even for Z quite small. We note second, as a far more significant matter, that some recent work by Englert and Schwinger (1984, 1985) uses TF theory as a starting point, but attempts to go well beyond it. The hope of the authors is not simply to obtain the first two corrections to the energy, in an expansion in powers of $Z^{-1/3}$, corrections which come from the inner electrons and from the bulk of the electrons, but to obtain the corrections associated with the surface electrons; one obtains at the same time corrections to $n(\mathbf{r})$. Although their fractional contribution to the total energy of the atom is not especially great, the surface electrons are, of course, of great significance, since they play the dominant role in the formation of molecules and in low-energy scattering processes. The modified version is much more complicated than the TF formulation, but preserves the essential simplifying feature of TF theory, namely, that one does not solve for a wave function of many variables but for $n(\mathbf{r})$. The modified version will therefore surely be simpler to use, for a sufficiently complicated system, than Hartree-Fock theory. We shall not discuss the modified version, since it lies well outside the range of normal TF theory, but wish simply to alert the reader to the possibility that a significant breakthrough may be in the offing.

II. NOTATION

Our primary concern will be with various energies, and a comment on the notation used for the different energies will therefore be useful. The symbol T denotes the kinetic-energy operator $-(\hbar^2/2m)\sum_i \nabla_i^2$, where the sum is over the different particles. The symbol $\tilde{E}[n]$ represents the energy of the system as a functional of the number density $n(\mathbf{r})$. The symbol $\tilde{E}(x)$, with no subscript and with x denoting one or more coordinates, represents an approximation, usually arrived at by some semiclassical argument, to the full Hamiltonian H. The symbol $\tilde{E}(x)$, with $\tilde{E}$ having one or more subscripts, represents one term in H, either the term as it actually appears in H or an approximation; in particular, the subscripts K, V, e, and ν refer to kinetic energy, potential energy, electron, and nucleus, respectively. Thus $\tilde{E}_K(x)$ and $\tilde{E}_V(x)$ refer to kinetic-energy and potential-energy functions, respectively, while $\tilde{E}_{e\nu}(x)$ and $\tilde{E}_{ee}(x)$ are particular potential-energy functions, namely, those associated with the electron-nucleus and electron-electron interactions, respectively. We shall sometimes use $V(x)$ rather than $\tilde{E}_V(x)$ for a potential. We shall use ϵ_F to represent the Fermi energy. This is not quite a contradiction of our convention that total energies do not have a subscript, since ϵ_F is the energy of an individual electron rather than of the entire system; in any event, ϵ_F is the usual convention. The symbol E, with or without a subscript, denotes not a function but a numerical value of some energy. E without a subscript is the total ground-state energy of the system, the minimum value of the true Hamiltonian, of $\tilde{E}[n]$ or of $\tilde{E}(x)$, while E_K, E_V, E_{ee}, and E_{ev}, for example, are the values of $\tilde{E}_K[n]$, $\tilde{E}_V[n]$, $\tilde{E}_{ee}[n]$, and $\tilde{E}_{ev}[n]$, respectively, for the $n(\mathbf{r})$ that minimizes $\tilde{E}[n]$.

In the discussion of molecules, energy functions that differ from their atomic counterparts are indicated by the inclusion of a prime. The subscript TF is sometimes used when there is the possibility of confusion between a TF energy and some other energy.

It is the hope—the expectation—of the author that only initially will the notation seem to be more difficult to grasp than some of the proofs.

A note on references: while an attempt has been made to include the latest references, a number of outdated (and even incorrect) references have also been included, not simply as a matter of proper accreditation (and "decreditation"), and not only for their historical interest, but because a knowledge of earlier developments often leads to a better understanding and reduces the mystery in the procedures used in later developments. Furthermore, it is not uncommon for ideas to be concentrated on in earlier papers and details in later papers.

III. PRELIMINARIES

A. The uncertainty principle

1. The usual form

It is well known that the uncertainty principle lies at the heart of quantum mechanics. We let $\langle\ \rangle$ represent an expectation value for an arbitrary normalized wave function, and Δf the root-mean-square deviation of f for f an arbitrary function, that is,

$$\Delta f \equiv \langle (f-\langle f\rangle)^2\rangle^{1/2} .$$

We then have the rigorous result that for an arbitrary normalized wave function for a particle in a three-dimensional space

$$\Delta x\,\Delta p_x \geq \hbar/2 , \qquad (3.1)$$

with similar inequalities for the other Cartesian coordinates and momenta. These results enable us to obtain a lower bound on the product $\langle \mathbf{p}^2\rangle\langle \mathbf{r}^2\rangle$ (Heisenberg, 1927). If we work in a frame in which the center of mass has zero momentum and is at the origin, so that $\langle \mathbf{p}\rangle = \langle \mathbf{r}\rangle = 0$, we have $\langle \mathbf{p}^2\rangle = \langle (\mathbf{p}-\langle \mathbf{p}\rangle)^2\rangle \equiv (\Delta\mathbf{p})^2$ and $\langle \mathbf{r}^2\rangle = \langle (\mathbf{r}-\langle \mathbf{r}\rangle)^2\rangle \equiv (\Delta\mathbf{r})^2$. It follows that

$$\begin{aligned}\langle \mathbf{r}^2\rangle\langle \mathbf{p}^2\rangle &= [(\Delta x\,\Delta p_x)^2 + \cdots\,] \\ &\quad + \{\{(\Delta x\,\Delta p_y)^2 + (\Delta y\,\Delta p_x)^2\} + \cdots\,\} \\ &\equiv [A] + \{B\} .\end{aligned}$$

The use of Eq. (3.1) immediately gives us $[A] \geq 3(\hbar/2)^2$ and, further, enables us to bound $\{B\}$. We have

$$\begin{aligned}\{B\} &= \{(\Delta x\,\Delta p_y)^2 + (\Delta y\,\Delta p_x)^2 + \cdots\,\} \\ &\geq (\hbar/2)^2\{\{(\Delta x/\Delta y)^2 + (\Delta y/\Delta x)^2\} + \cdots\,\} \\ &\geq 6(\hbar/2)^2 ,\end{aligned}$$

where in the last step we used $(a/b)^2+(b/a)^2 \geq 2$, valid for any real numbers a and b. We therefore have $\langle \mathbf{r}^2\rangle\langle \mathbf{p}^2\rangle \geq (9/4)\hbar^2$, or

$$\langle \mathbf{p}^2/2m\rangle \geq (9/4)\hbar^2/(2m\langle \mathbf{r}^2\rangle) . \qquad (3.2)$$

This is the form we shall normally use. [For a single particle not in a three-dimensional but a D-dimensional space, we need merely replace $9=3^2$ in Eq. (3.2) by D^2. With D thought of as a parameter and as large, this result is of interest in connection with the $1/D$ expansions that have been so popular recently in quantum field theory and in a number of other areas. For an elementary review, see Witten (1980). See also Herschbach (1989) and references therein.] To within a numerical coefficient of order unity, the *legitimately* derived bound (3.2) is obtained very simply as an estimate of $\langle \mathbf{p}^2/2m\rangle$ if we use

$$p \approx \Delta p \gtrsim \hbar/\Delta r \approx \hbar/r , \qquad (3.3)$$

where $p\equiv|\mathbf{p}|$, $\Delta p \equiv |\Delta\mathbf{p}|, r\equiv|\mathbf{r}|$, and $\Delta r \equiv |\Delta \mathbf{r}|$. The crude form of Eq. (3.3) is suggested by Eq. (3.1) and its Cartesian analogs, but has no proper justification. The crude form is, nevertheless, normally the simplest form to apply, and it is the form we shall often use. We shall return to this point in the following paragraph. We stress the fact that the expectation values in Eq. (3.2) are with respect to an *arbitrary* normalized wave function, which need bear no relation to the physical wave function for the problem under consideration.

That the relationships in Eq. (3.3) have no rigorous basis is clear. The more important observation, one that has been pointed out and stressed by Lieb (1976), is that the classical Hamiltonian combined with the *rigorous* form in Eq. (3.2) does *not* encompass, even qualitatively, the full physical content of the Schrödinger equation. Thus, in studying the hydrogen atom or a hydrogenlike ion, one can choose a normalized function $\psi(\mathbf{r})$ to be sharply peaked at two widely separated points, one at the origin and one at a great distance L from the origin. With the integral over each peak normalized to 1/2, the distant peak will cause $\langle \mathbf{r}^2\rangle$ to be close to $L^2/2$, which can be arbitrarily large, so that the lower bound on $\langle \mathbf{p}^2/2m\rangle$ will be arbitrarily small. On the other hand, the peak near the origin will cause $\langle -Ze^2/r\rangle$ to be arbitrarily large and negative. Formally, therefore, the inequality (3.2) cannot be used to prove that a hydrogen atom or hydrogenlike ion is stable, that is, that the energy is bounded from below. To the author at least, however, it seems fair to say that despite its formal weakness the usual form in which the uncertainty principle is used, Eq. (3.3), can represent one of the most powerful tools available to the physicist if he wishes to make quick rough estimates. Indeed, if the problem is reasonably simple, that is, if the physics is reasonably well understood—which will be the case not only for one-electron atoms, but, for example, for normal many-electron atoms, for many-electron atoms in strong magnetic fields, for white dwarfs, and for neutron stars—one has to be not simply perverse but clever to obtain a bad answer, and the physical flaw in the argument leading to a bad answer may well be obvious; in the example discussed just above, for example, it would take very-high-momentum components to have a $\psi(\mathbf{r})$ with one or more sharp peaks.

On the other hand, if the physics is not well understood, or if one is interested in rigorous proofs or in bounds, it is quite clear that one must proceed differently. One possibility is to use a stronger version of the uncertainty principle, the Sobolev inequality (Sobolev, 1938, 1963), which we shall now discuss briefly.

2. The Sobolev inequality

The Sobolev inequality represents a stronger version of the uncertainty principle, or, more precisely, a stronger version of the lower bound on $\langle \mathbf{p}^2/2m \rangle$ than that provided by Eq. (3.2). As we shall show in Sec. III.B, the use of this inequality *does* enable one to prove rigorously that a hydrogenlike ion is stable, and, further, provides a lower bound on the ground-state energy. However, the primary reason for our interest in the inequality is that its beautiful many-particle fermion extension plays an essential role in by far the simplest proof yet given of the stability of matter. For matter with its large number of (charged) fermions, and even more so for a system with a larger number of positively and negatively charged point bosons, the determination of the ground-state energy and wave function is a very difficult problem with many subtle aspects, and an approach based on Eq. (3.2) could very easily give incorrect results. (Even for the boson case, however, it can be shown, though we shall not do so, that the results can be most easily *interpreted*—though not readily until *after* the calculation has been completed—in terms of the usual uncertainty-principle formulation, giving an enormous increase in one's physical understanding.)

We shall only sketch the determination of a bound on the kinetic energy E_K of a single particle in terms of an integral involving the one-particle number density $n(\mathbf{r})$; details can be found in Lieb's review paper (Lieb, 1976). It can be shown rigorously—but we shall simply assume—that there exists a function, to be denoted by $\psi_{\min}(\mathbf{r})$, which minimizes the ratio

$$Q \equiv \int |\nabla\psi(\mathbf{r})|^2 d\mathbf{r} \Big/ \left[\int |\psi(\mathbf{r})|^6 d\mathbf{r}\right]^{1/3} . \tag{3.4}$$

The differential equation satisfied by $\psi_{\min}(\mathbf{r})$ follows easily from the calculus of variations on setting the variation of Q equal to zero. One is spared any numerical calculation by the pleasant circumstance that the (spherically symmetric) solution $\psi_{\min}(r)$ of the differential equation can be obtained in (simple) analytic form, the r-dependent factor being $(1+r^2)^{-1/2}$; that $\psi_{\min}(r)$ is not normalizable is irrelevant with regard to the minimization of Q. Insertion of $\psi_{\min}(r)$ into the ratio in Eq. (3.4) gives, for the minimum value of the ratio,

$$K_s = 3(\pi/2)^{4/3} \approx 5.478 . \tag{3.5}$$

We now have the Sobolev inequality

$$\int |\nabla\psi(\mathbf{r})|^2 d\mathbf{r} \ge K_s \left[\int |\psi(\mathbf{r})|^6 d\mathbf{r}\right]^{1/3} , \tag{3.6}$$

with K_s given in Eq. (3.5) and $\psi(\mathbf{r})$ arbitrary; $\psi(\mathbf{r})$ need be neither normalized nor the solution of any particular differential equation. If $\psi(\mathbf{r})$ is normalized, we can introduce the number density

$$n(\mathbf{r}) \equiv |\psi(\mathbf{r})|^2 , \tag{3.7}$$

which then satisfies

$$\int n(\mathbf{r}) d\mathbf{r} = 1 , \tag{3.8}$$

and rewrite (3.6) as

$$\langle \mathbf{p}^2/2m \rangle \ge K_s(\hbar^2/2m) \left[\int n^3(\mathbf{r}) d\mathbf{r}\right]^{1/3} . \tag{3.9}$$

We now use the Hölder inequality—see, for example, Problem, 8.2 in Byron and Fuller (1970)—which states that

$$\int |f(x)g(x)| dx \le \left[\int |f(x)|^p dx\right]^{1/p} \left[\int |g(x)|^q dx\right]^{1/q}$$

for $p^{-1}+q^{-1}=1$ and $p \ge 1$. (This reduces to the Schwarz inequality for $p=q=2$.) Choosing $x=\mathbf{r}$, $f(x)=n(\mathbf{r})$, $g(x)=n^{2/3}(\mathbf{r})$, $p=3$, and $q=3/2$, one finds, using (3.8) and (3.9), that

$$\langle \mathbf{p}^2/2m \rangle \ge K_s(\hbar^2/2m) \int n^{5/3}(\mathbf{r}) d\mathbf{r} . \tag{3.10}$$

Having been obtained from (3.9) by means of a further inequality (the Hölder inequality), (3.10) gives a poorer bound on $\langle \mathbf{p}^2/2m \rangle$ than does (3.9); the interesting feature of the latter bound is that its integrand contains the same $n^{5/3}$ factor that appears in the integrand of the Thomas-Fermi estimate of the kinetic energy of a system of fermions, an essential element in the rigorous proof, based on TF theory, of the stability of matter (see Sec. VIII). The bound (3.10) can be improved by the replacement of K_s by $K_1 > K_s$; thus, rather than using the circuitous route of passing through (3.9) to arrive at (3.10), one proceeds directly, with K_1 defined as the minimum value of

$$\int |\nabla\psi(\mathbf{r})|^2 d\mathbf{r} \Big/ \int |\psi(\mathbf{r})|^{10/3} d\mathbf{r} .$$

One finds (Lieb, 1976)

$$K_1 \approx 9.578 . \tag{3.11}$$

As noted in Sec. III.B.1 below, (3.10), preferably with K_s replaced by K_1, can be used to provide a *lower* bound on the ground-state energy of a hydrogen atom. As a mnemonic, note that the assumption that there exists an inequality of the form

$$\int |\nabla\psi(\mathbf{r})|^2 d\mathbf{r} \geq K' \int n^{\gamma}(\mathbf{r}) d\mathbf{r} ,$$

with K' dimensionless and $\psi(\mathbf{r})$ normalized, demands, on dimensional grounds, that $\gamma=5/3$.

B. The hydrogen atom and hydrogenlike ions

1. The nonrelativistic approximation

We consider the hydrogen atom and hydrogenlike ions [even though a one-electron problem is not fit subject matter for the (statistical) TF model] since the approach to be used—the usual approach—is and later will be readily adapted to the problems of the estimation of the energy of a many-electron atom in the laboratory or in the intense magnetic field at the surface of a neutron star, of a neutron star itself, and of a white dwarf. The nonrelativistic Hamiltonian is

$$H(\mathbf{r},\mathbf{p})=(p^2/m_e)-Ze^2/r ,$$

where m_e the electron mass and Ze the nuclear charge. (We have dropped a factor of 1/2 in the kinetic-energy term. Since we wish to emphasize the physical picture rather than numerical details, we shall often set constants such as 1/2, $3^{1/2}$, or π equal to 1, unless doing so changes the result qualitatively. In the old days at MIT, these were known by those of us who had the pleasure of working with him as Weisskopf units.) Classically, $\mathbf{r}$ and $\mathbf{p}$ are independent and therefore, with $\mathbf{p}$ fixed, r can approach zero, the energy can approach $-\infty$—problems with OPEC would disappear and cold fusion would, even if possible, not be so exciting—and the atom is unstable. Quantum mechanically, we proceed by using the crude result (3.3) to write

$$p^2/m_e \approx \hbar^2/m_e r^2 .$$

We can therefore write

$$H(\mathbf{r},\mathbf{p}) \approx (\hbar^2/m_e r^2)-(Ze^2/r) \equiv \tilde{E}(r) . \tag{3.12}$$

Setting $d\tilde{E}/dr=0$ and inserting the values of r thereby obtained into Eq. (3.12) gives the desired results,

$$r(H\text{-like}) \approx a_0/Z, \quad E(H\text{-like}) \approx -Z^2(e^2/a_0) ,$$

where $a_0 \approx \hbar^2/m_e e^2$ is the Bohr radius. The a_0 factor for the radius r and the (e^2/a_0) factor for the ground-state energy E would follow from dimensional analysis alone. The success of the simple procedure just used is its correct prediction of the Z dependence of r and E. (The extension of the above procedure to the estimation of the lowest energy for an angular momentum quantum number l is trivial.) If we rewrite Eq. (3.12) as

$$\tilde{E}(R)=\tilde{E}_K(r)+\tilde{E}_V(r) ,$$

and let $E_K \equiv \tilde{E}_k(a_0/Z)$ and $E_V \equiv \tilde{E}_V(a_0/Z)$, we find that the expectation values E_K and E_V satisfy

$$2E_K+E_V=0$$

so that the approximations used have not altered the relation obtained from the virial theorem.

$E(H\text{-like})$ is finite for any finite Z, no matter how large. This is a consequence of the fact that the kinetic-energy operator [in the approximation given in Eq. (3.12)] increases as $1/r^2$ as $r \sim 0$, while the potential-energy operator increases only as $1/r$. For an attractive $1/r^3$ potential, the system would be unstable independent of the strength of the coefficient of the $1/r^3$ potential. For an attractive $1/r^2$ potential, the system would be stable for a small coefficient but unstable for a sufficiently large coefficient. In the relativistic case, the effective kinetic-energy operator for a very deep energy level will be approximately pc and therefore proportional to $1/r$. It follows, as is well known and as will be spelled out in the following subsection, that in relativistic theory the stability of a system with an attractive $1/r$ potential will be determined by the size of the coefficient; a system with an attractive $1/r^2$ potential will be unstable independent of the strength of the potential.

A simple yet interesting application of the Sobolev inequality is the determination of a lower bound (the more difficult bound) on the ground-state energy E of a hydrogenlike ion (Lieb, 1976). We simply sketch the argument. Writing $\langle H \rangle = \langle p^2/2m \rangle - \langle Ze^2/r \rangle$, we find that the use of (3.9) and of $\langle -Ze^2/r \rangle = -e^2 \int [n(r)/r] d^3r$ gives a lower bound on E in the form of a functional $\tilde{E}[n]$ which contains no gradients. Varying $\tilde{E}[n]$ subject to the normalization condition Eq. (3.8) gives an equation for $n(r)$ that can be solved trivially. [For later reference, we note that the $n(r)$ obtained vanishes *identically* beyond some given value of r, and that the Lagrange multiplier used in connection with the normalization condition does *not* vanish. We are here concerned not with the true hydrogen problem nor even with the hydrogen problem in the TF approximation, but these properties—especially the vanishing of $n(\mathbf{r})$—should give us pause; they are properties quite different from those that arise in a TF treatment of a neutral atom.] The lower bound obtained by Lieb in this simple analysis is off by only 33%.

We note that it would make little difference if the distance r of the electron from the nucleus were reinterpreted as the radius r of a sphere within which the electron is confined; this viewpoint simplifies the transition to the many-electron atom. We also note that the ground-state energy of the neutral helium atom can be approximated in much the same way as it was approximated for H-like atoms. The Pauli principle does not play a role other than, effectively, to require that in the ground state one electron have spin up and the other spin down. [In the usual treatment the only new wrinkle is the approximation of $1/r_{12}$ by $1/(r_1+r_2)$, which is physically reasonable since the two electrons repel one another.] As we go to Li and beyond, however, the Pauli principle plays an essential role.

2. A note on the relativistic problem and the question of collapse

The analysis of a hydrogenlike ion in its ground state in the nonrelativistic approximation gives

$$v/c=p/m_ec\approx\hbar/(m_ecr)\approx Z\hbar/(m_eca_0)=\alpha Z\ ,$$

where $\alpha\equiv e^2/\hbar c$. For the nonrelativistic approximation to be consistent we must therefore demand that $\alpha Z\ll 1$. If this condition is not satisfied, we can study the hydrogenlike ions along the above lines, that is, by using Eq. (3.3), if we are willing to make certain further approximations, including the neglect of the spin of the electron. Making these approximations, we write

$$H(\mathrm{rel};\mathbf{r},\mathbf{p})=[(m_ec^2)^2+(pc)^2]^{1/2}-Ze^2/r\ ,$$

and define

$$\tilde{E}(\mathrm{rel};r)\equiv H(\mathrm{rel};r,\hbar/r)\ .$$

Minimization of $\tilde{E}$(rel;r) with respect to r and the substitution of the value of r thereby obtained into $\tilde{E}$(rel;r) gives

$$r(\mathrm{rel};H\text{-like})\approx(a_0/Z)(1-\alpha^2Z^2)^{1/2}\ ,$$

$$E(\mathrm{rel};H\text{-like})\approx mc^2(1-\alpha^2Z^2)^{1/2}\ .$$

The expressions for r and E cease to have meaning for $\alpha Z>1$, because of the factor $(1-\alpha^2Z^2)^{1/2}$. (This same factor occurs often in a correct treatment of the Dirac equation. The fact that our approximate treatment gave exactly this factor is accidental. Had we used $p\rightarrow s\hbar/r$ with $s\neq 1$, we would not have obtained precisely that factor.) A mathematician might say that H(rel;$\mathbf{r}$,$\mathbf{p}$) is no longer Hermitian, or, better, that it has no self-adjoint extension. A physicist might say that is not relevant, since the nucleus is not really a point and has finite mass, and, further, there are quantum-electrodynamic corrections. Further, the Z of a nucleus is limited from above to well below 137 by the nature of nuclear forces. One does not therefore expect to observe collapse for hydrogenlike ions. However, as stressed by Lieb and Yau (1988a, 1988b), as one approaches conditions under which a simple theory predicts collapse, one expects that dramatic changes in the theory will be necessary to provide an adequate description of the system. Thus, for example, in the present context, if a pair of heavy nuclei are brought very close together by means of a heavy-ion accelerator, "strange" behavior, such as positron production, occurs (Cowan *et al.*, 1985; Cowan and Greenberg, 1987).

That αZ of order unity is the value at which strange behavior begins can be seen more easily than by the above analysis. Since strange behavior can be expected only if the speed of the electron is of order c, we can study the ultrarelativistic limit, with $p\gg m_ec$ and $\tilde{E}_K(r)\approx pc\approx\hbar c/r$. We then have, in a treatment that is even more cavalier than for the nonrelativistic case,

$$H(\mathrm{ultra};\mathbf{r},\mathbf{p})\approx\hbar c(1-\alpha Z)/r\equiv\tilde{E}(\mathrm{ultra};r)\ .$$

$\tilde{E}$(ultra;r) has no minimum for $\alpha Z>1$, and we then expect the one-electron ion, for the point-nucleus model assumed, to collapse. [We note that J. D. Garcia (1986) has recently given a simple argument for the breakdown at $\alpha Z=1$; he uses classical relativistic mechanics to study *circular* orbits, whose properties can be expressed in terms of the orbital angular momentum L, and quantizes L using Bohr theory.] Collapse considerations are of very great importance in the neutron star and white dwarf, to be considered shortly—the collapse there is due to the cumulative effect of very many (gravitational) interactions rather than to the great strength of an individual pair interaction—and the fact that H(ultra;$\mathbf{r}$,$\mathbf{p}$) gives roughly the same collapse condition as does the generally more reliable H(rel;$\mathbf{r}$,$\mathbf{p}$) suggests that the ultrarelativistic approximation may be sufficient for a rough estimate of the collapse condition for a many-body system. We shall use that approximation in Sec. IV.A.2 to study the conditions for the collapse of a heavy atom, assumed to have uniform density, and in Sec. VI.D to study the conditions for the collapse of neutron stars and of white dwarfs. (With the observation and data analysis of Supernova 1987a having changed the concept of the formation of a neutron star via the collapse of a star from a fantastic theory to a fantastic fact, one need hardly justify studies of the conditions for collapse.) Results have been obtained by Lieb and Yau (1988a, 1988b) and Martin (1988a, 1988b); see also Thirring (1986). First, though, we obtain a rigorous bound, for a model Hamiltonian for a heavy atom, on the strength of the coupling constant $\alpha=e^2/\hbar c$.

As noted above, it was only very recently realized that, under certain assumptions, a knowledge of the *nonrelativistic* ground-state energy $E_{NR}(m_0,N,\gamma_j)$ of a system of N particles of mass m_0, interacting via potentials characterized by coupling constants γ_j, can be a very useful tool in the analysis of conditions for the collapse of the corresponding relativistic problem. This makes it possible to extend considerations of collapse from the hydrogen atom to many-body systems. We shall here confine ourselves to a very simple approach, that of Martin (1988a, 1988b), which provides bounds on the collapse conditions. To be precise, we make the unjustified but interesting assumption that the dominant relativistic effect is obtained by replacing the nonrelativistic Hamiltonian

$$H_{NR}(m_0,N,\gamma_j)=Nm_0c^2+\sum_i(p_i^2/2m_0)+V(\gamma_j)$$

by the relativistic Hamiltonian—the term semirelativistic is used sometimes—

$$H_R(m_0,N,\gamma_j)=\sum_i(p_i^2c^2+m_0^2c^4)^{1/2}+V(\gamma_j)\ .$$

[For $N=1$ and $V=-Ze^2/r$, for a nucleus of infinite mass, it is then known that collapse occurs for $\alpha Z\geq 2/\pi$ (Herbst, 1977), not all that different from the condition

$\alpha Z\ge 1$ for the Dirac equation.] The trivial operator inequality

$$(p_i^2c^2+m_0^2c^4)^{1/2}\le \tfrac{1}{2}[(p_i^2c^2+m_0^2c^4)/(mc^2)]+\tfrac{1}{2}mc^2$$

follows from $(a^{1/2}-b^{1/2})^2\ge 0$ with $a=(p_i^2c^2+m_0^2c^4)/(2mc^2)$ and $b=mc^2/2$. It is valid for arbitrary m and leads immediately to

$$H_R(m_0,N,\gamma_j)\le \tfrac{1}{2}Nmc^2+\tfrac{1}{2}N(m_0^2c^2/m) +H_{NR}(m,N,\gamma_j)-Nm_0c^2 \ .$$

For inverse-square-law forces it follows by scaling (let $m\to\lambda m$ and $r_i\to r_i/\lambda$) that

$$E_{NR}(m,N,\gamma_j)=-mF(N,\gamma_j) \ ,$$

with γ_j the Coulomb or gravitational coupling constants. With the upper bound (the bound simple to obtain) $\bar{E}_{NR}$ on E_{NR} providing a lower bound $\underline{F}$ on F, we arrive at the upper limit on the relativistic ground-state energy

$$E_R(m_0,N,\gamma_j)\le m[\tfrac{1}{2}Nc^2-\underline{F}(N,\gamma_j)] +\tfrac{1}{2}Nm_0^2c^2/m-Nm_0c^2 \ .$$

Since m can be arbitrarily large, collapse will occur if

$$\underline{F}(N,\gamma_j)>\tfrac{1}{2}Nc^2 \ .$$

With N replaced by Z and γ_j by the fine-structure constant α (and m_0 by m_e), we apply this to a neutral atom, using

$$\underline{F}=-\bar{E}_{NR}(m_e,Z,\alpha)/m_e =CZ^{7/3}\alpha^2c^2, \quad C>0.447 \ .$$

(The bound on C is obtained using known results for $\bar{E}_{NR}$ and scaling techniques.) The $Z^{7/3}$ factor is dictated by the desire to have the same form for all Z and the fact that, as given by TF theory, the Z dependence for large Z is $Z^{7/3}$. We thus have collapse for a relativistic neutral atom (or a collection of neutral atoms) for

$$Z^{4/3}\alpha^2>(2\times 0.447)^{-1}, \quad \text{or } \alpha>1.05Z^{-2/3} \ .$$

Similar methods can be applied to neutron stars and white dwarfs. There is a very brief discussion of the collapse condition for a boson star at the very end of Sec. VI.A.

We shall henceforth almost always and unless otherwise noted restrict our considerations to situations for which the nonrelativistic approximation is expected to be reliable, or at least meaningful. However, before closing this subsection on relativistic effects in one-electron and many-electron ions, we observe that the simple arguments above may have profound consequences with regard to the possibility of constructing a relativistic TF-like theory. As noted by Lieb, the instability in relativistic theory of an electron in the field of a point nucleus of very high Z strongly suggests that it will not be possible to obtain a relativistic TF-like theory, for a TF-like theory should get better as Z is increased. If these remarks suggest that one cannot construct a relativistic TF-like theory of the universality and simplicity of nonrelativistic TF theory, the remarks by no means preclude the possibility that TF theory itself, or a relativistic modification, can be useful in a treatment of relativistic effects. Thus, for Z less than perhaps 80, one might treat relativistic effects as a perturbation on normal TF theory. For somewhat higher Z, one might avoid the singularity by accounting for the finite size of the nucleus; for $Z\le 170$, "strange" behavior would not yet have begun. As a far more significant example, consider the conditions for the collapse of a white dwarf. We shall examine this in some detail in Sec. VI. Here, we simply note that by far the dominant contributions to the energy are the kinetic energy of the electrons and the gravitational energy of the nuclei, the sum of the two terms constituting the zeroth-order Hamiltonian $H^{(0)}$. Since the nuclei are moving slowly, the gravitational interaction of a pair is simply the Newtonian potential. As the number of electrons and nuclei approach the critical number at which collapse occurs, the electrons move with speeds approaching the speed of light, but one would expect that the only relativistic effect of significance would be the kinematic one, so that the kinetic energy of the ith electron would not be $p_i^2/2m_e$, but $t_i\equiv(p_i^2c^2+m_e^2c^4)^{1/2}$, or, more simply, p_ic. H_0 is then a sum of Newtonian potentials and of the t_i. Since the number of particles involved here is enormous, we have a situation in which the TF solution to the problem defined by $H^{(0)}$ is effectively exact. To be more precise, consider, for example, a white dwarf containing electrons of mass m_e and protons of mass m_p. We neglect the kinetic energy of the protons, all Coulomb interactions—they saturate while the gravitational interactions do not—and the gravitational interactions of the electrons. (The justification of these approximations will be considered in more detail in the treatment of white dwarfs in Sec. VI.) Finally, we neglect the m_e term in t_i, defined just above, replacing t_i by p_ic. (This is justified by the fact that the spectrum with t_i replaced by p_ic extends to $-\infty$ if the spectrum with t_i extends to $-\infty$, so that the condition for collapse is not affected by the replacement $t_i\to p_ic$. See Lieb and Thirring, 1984, on which the present discussion is based.) The Hamiltonian is then given by

$$H_R=\sum_i p_ic-\sum_{i<j}\sum Gm_p^2/r_{ij} \ .$$

We then construct the relativistic TF energy functional corresponding to H_R. The procedure is very similar to that used in constructing the standard nonrelativistic TF energy functional, described in Sec. IV.B below; in constructing the kinetic-energy functional, one uses p_ic rather than $p_i^2/2m_e$. Let $N_{\text{crit TF}}$ be the critical number for which the TF energy functional is unbounded from below, that is, the number of protons, or electrons, for which collapse is first possible. The (numerical) determination of $N_{\text{crit TF}}$ is rather simple, and its value is that determined by Chandrasekhar (1931a, 1931b) and Landau (1932). $N_{\mathrm{crit\ TF}}$ is expected to equal the true value N_{crit}—we are dealing with very large numbers. Lieb and Thirring (1984) have shown rigorously that $N_{\mathrm{crit\ TF}}$ is a lower bound on N_{crit}, and Lieb and Yau (1987a, 1987b) showed that the Chandrasekhar theory of stellar collapse is the quantum-mechanical limit as the number N of protons or electrons approaches infinity and the gravitational constant G approaches zero; fixing $GN^{2/3}$ and taking the limits, one obtains Chandrasekhar's results.

C. The virial theorem and some extensions

1. Systems with one characteristic length

The virial theorem is an immediate consequence of Newton's second law or, for our purposes, of the Schrödinger equation. For a system of particles with vanishing probability of being found outside a given volume of space and interacting via two-particle forces $\mathbf{F}_{ij}(\mathbf{r}_{ij})=-\nabla_i V_{ij}(\mathbf{r}_{ij})$, with no external forces, one finds

$$2E_K=\left\langle \sum \mathbf{r}_{ij}\cdot\nabla_i V_{ij}(\mathbf{r}_{ij})\right\rangle , \tag{3.13}$$

where the sum is over all pairs of particles; in classical physics the angular brackets represent a time average, but in the present quantum-mechanical context, with the particles in a given state, the angular brackets represent, as almost always in this article, an expectation value. The virial theorem of Eq. (3.13) reduces to a particularly simple form if $V_{ij}(\mathbf{r}_{ij})=C_{ij}r_{ij}^p$, with $r_{ij}\equiv|\mathbf{r}_i-\mathbf{r}_j|$ the separation, namely, $2E_K-pE_V=0$. For Coulomb or gravitational interactions, that is, for $p=-1$, one has the famous result

$$2E_K+E_V=0 , \tag{3.14}$$

where E_V is the sum of the expectation values of the two-particle interactions. One normally demands of an approximation technique that it preserve the virial theorem result; this was found to be the case for the simple uncertainty-principle treatment of hydrogenlike ions in Sec.III.B.1 and will be the case for the Thomas-Fermi approximation for heavy atoms, as well as for almost all approximate treatments of white dwarfs and neutron stars, for which the kinetic energy originates in the uncertainty principle and exclusion principle, and of stars for which the kinetic energy is associated with thermal motion.

Let us now assume that in some approximation we have reduced our one-body or many-body Hamiltonian to a simple function of some one variable R, of the form

$$\tilde{E}(R)=\tilde{E}_l(R)+\tilde{E}_m(R)\equiv(C_l/R^l)+(C_m/R^m) , \tag{3.15}$$

with $l\neq m$, C_l and C_m known constants, and $(lC_l/mC_m)<0$. Equating $d\tilde{E}(R)/dR$ to zero gives the equilibrium value R_{eq} of R,

$$R_{\mathrm{eq}}\equiv(-lC_l/mC_m)^{1/(l-m)} .$$

The use of this value of R_{eq} enables us to determine E, the equilibrium value $\tilde{E}(R_{\mathrm{eq}})$ of $\tilde{E}(R)$. More interesting for present purpose is that setting

$$d\tilde{E}(R)/dR=-(1/R)[l\tilde{E}_l(R)+m\tilde{E}_m(R)]$$

equal to zero gives

$$lE_l+mE_m=0 , \tag{3.16}$$

where $E_l\equiv\tilde{E}_l(R_{\mathrm{eq}})$ and $E_m\equiv\tilde{E}_m(R_{\mathrm{eq}})$. The point to note is that the ratio of E_l to E_m depends upon l and m but is *independent* of C_l and C_m. For $\tilde{E}_l(R)=\tilde{E}_K(R)\propto 1/R^2$ and $\tilde{E}_m(R)=\tilde{E}_V(R)\propto 1/R$, that is, for $l=2$ and $m=1$, we have the usual virial result, Eq. (3.14). For $\tilde{E}_l(R)=\tilde{E}_{Kz}(R)=C(B)/R^6$ with $C(B)$ an arbitrary function of some parameter B and $\tilde{E}_m(R)=\tilde{E}_V(r)\propto 1/R$, which will be seen later to be the case for an atom in a strong uniform magnetic field $\mathbf{B}$, with $\tilde{E}_{Kz}(R)$ the kinetic-energy function associated with motion parallel to the field, we have

$$6E_{Kz}+E_V=0 . \tag{3.17a}$$

We shall comment on this relation in Sec. VII.

The relationship (3.14) is of some interest for the hydrogen atom but of much greater interest for an atom with two or more electrons, since the latter problem is not a solvable one. For the many-electron atom it is often convenient to decompose E_V, writing

$$E_V=E_{ev}+E_{ee} , \tag{3.17b}$$

where E_{ev} and E_{ee} are the expectation values of the sums of the electron-nucleus and electron-electron interactions, respectively. With this notation, Eq. (3.14) becomes

$$2E_K+E_{ev}+E_{ee}=0 . \tag{3.18}$$

It would be exceedingly useful to be able to deduce the ratio of E_{ev} and E_{ee} on the basis of some simple principle. One cannot use the two-characteristic-lengths approach of Sec. III.C.2 below, because each of the two terms is of the same order, Z^2e^2/R, where R is the characteristic dimension of the atom. Indeed the ratio is not even known, except in the limit $Z\sim\infty$; the same remark obtains for atoms in magnetic fields. There *is* a simple principle, due to A.R.P. Rau (unpublished) and Thirring (1983), which gives the correct ratio in the $Z\sim\infty$ limit. We shall discuss this principle in Secs. V.B.2.c and VII.B.2.

If particles are confined to a region of space of volume τ by a pressure P, the forces are no longer simply the two-particle forces $\mathbf{F}_{ij}$ but now include forces exerted by the walls. One then finds (Clayton, 1983) that the result for the arbitrary potentials, Eq. (3.13), and the result for Coulomb potentials, Eq. (3.14), must be replaced by

$$2E_K=3P_\tau+\left\langle \sum \mathbf{r}_{ij}\cdot\nabla_i V_{ij}(\mathbf{r}_{ij})\right\rangle \tag{3.19a}$$

and

$$2E_K+E_V=3P_\tau \;, \tag{3.19b}$$

respectively. The concept of an external pressure is useful not only when one considers particles in a container but also when one considers an infinite number of particles with a specified constant number density. This occurs, for example, in the study of a system of charged bosons.

For the energy of a simple function of a distance R, as in Eq. (3.15), we have seen that it can be trivial to obtain a relationship between components of the energy. It is also often simple to obtain such a relationship when the energy is a functional of the number density $n(\mathbf{r})$. With no attempt at generality, we assume that $\tilde{E}[n]$ has the form

$$\begin{aligned}\tilde{E}[n]&=C_l\int n^l(\mathbf{r})d\mathbf{r}+C_f\int n(\mathbf{r})f(\mathbf{r})d\mathbf{r}\\&\quad+C_g\int\int n(\mathbf{r})n(\mathbf{r}')g(\mathbf{r},\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'\\&\equiv\tilde{E}_l[n]+\tilde{E}_f[n]+\tilde{E}_g[n]\;,\end{aligned} \tag{3.20a}$$

where the C's are arbitrary constants and where $f(\mathbf{r})$ and $g(\mathbf{r},\mathbf{r}')$ are arbitrary other than for the restrictions that $g(\mathbf{r},\mathbf{r}')=g(\mathbf{r}',\mathbf{r})$ and that the integrals exist. We further assume that the total number of particles is fixed at N, so that

$$\int n(\mathbf{r})d\mathbf{r}=N\;.$$

Finally, we assume that $n(\mathbf{r})>0$ for all $\mathbf{r}$ other than at the point at infinity, where it is zero. (We shall, unfortunately, have to belabor this seemingly trivial but actually very important matter in Sec. IV, and we shall spare the reader a discussion of the matter here.) We introduce a new functional $F[n]$ defined by

$$F[n]=\tilde{E}[n]+\mu\left[\int n(\mathbf{r})d\mathbf{r}-N\right]\;,$$

with μ a Lagrange multiplier. Then we proceed to extremalize the energy with respect to an arbitrary variation $\delta n(\mathbf{r})$ of $n(\mathbf{r})$ by setting $\delta F/\delta n=0$ and obtain

$$lC_l n^{l-1}(\mathbf{r})+C_f f(\mathbf{r})+2C_g\int n(\mathbf{r}')g(\mathbf{r},\mathbf{r}')d\mathbf{r}'+\mu=0\;.$$

Multiplication by $n(\mathbf{r})$ and integration over $\mathbf{r}$ gives the sought-for relation among the energy components (though it still involves μ) for the total energy an extremum—normally a minimum—namely,

$$lE_l+E_f+2E_g+\mu N=0\;. \tag{3.20b}$$

With C_l appropriately chosen, $\tilde{E}_l[n]$ represents, as will be seen later, the kinetic energy in the TF nonrelativistic theory, with $l=5/3$ in the absence of a magnetic field and $l=3$ in the presence of an intense magnetic field, while $\tilde{E}_l[n]$ with $l=4/3$ can represent either the kinetic energy in an ultrarelativistic TF-like approximation or the exchange potential energy contribution calculated by Dirac (1930), a correction to nonrelativistic TF theory. With $C_f f(r)=-Ze^2/r$, $\tilde{E}_f[n]=\tilde{E}_{ev}[n]$ represents the electron-nuclear interaction contribution. With $C_g g(\mathbf{r},\mathbf{r}')=(e^2/2)|\mathbf{r}-\mathbf{r}'|^{-1}$, $\tilde{E}_g[n]=\tilde{E}_{ee}[n]$ represents the electron-electron interaction. The relationship between the energy components is especially simple for $\mu=0$, which will later be seen to be true for some very important cases.

A second relationship between the energy components can often be obtained by using a scaling technique, as we shall show in Sec. V [see Eqs. (5.10) and (5.11)].

It is often the case, as in the treatment of the white dwarf in Sec. VI, that one proceeds in a perturbation-theoretic fashion. To allay any possible confusion, it may be useful to set up a straw man by questioning the validity of the virial theorem in a perturbation-theoretic approach. Assume that $H=H^{(0)}+V^{(1)}$, where $H^{(0)}=T+V^{(0)}$, where both $V^{(0)}$ and $V^{(1)}$ are Coulombic or gravitational potentials, and where $V^{(0)}$ is attractive while $V^{(1)}$ can be attractive or repulsive. The energy components $E_K^{(0)}$ and $E_V^{(0)}$ of the minimum energy $E^{(0)}=E_K^{(0)}+E_V^{(0)}$ associated with $H^{(0)}$ satisfy the virial theorem in the form $2E_K^{(0)}+E_V^{(0)}=0$. With $V^{(1)}$ treated as a perturbation, there is a correction $E_V^{(1)}$, so that $E^{(1)}$, the ground-state energy associated with H through terms of first order in $V^{(1)}$, is given by $E^{(1)}=E_K^{(0)}+E_V^{(0)}+E_V^{(1)}$. We clearly do not have $2E_K^{(0)}+[E_V^{(0)}+E_V^{(1)}]$ equal to zero, but the virial theorem remains valid nevertheless, for there is a readjustment of the zeroth-order energy between kinetic- and potential-energy components, with $E^{(0)}$ fixed. To make the discussion more concrete, consider the simple example

$$\begin{aligned}\tilde{E}(R)&=\left[\frac{A}{R^2}-\frac{B}{R}\right]+\frac{C}{R}\\&\equiv\tilde{E}^{(0)}(R)+V^{(1)}(R)\;,\end{aligned}$$

where $B\gg|C|$. (With A/R^2 the kinetic energy and $-B/R$ and C/R the gravitational and Coulombic-potential energies, respectively, this equation arises in studies of white dwarfs.) The minimum energy $E^{(0)}(R_{\rm eq}^{(0)})$ associated with $\tilde{E}^{(0)}(R)$ is stationary with respect to small changes in the equilibrium radius $R_{\rm eq}^{(0)}$, but the kinetic- and potential-energy components of $E^{(0)}(R_{\rm eq}^{(0)})$ are not separately stationary under the small change in the equilibrium radius $(-2AC/B^2)$ induced by the perturbation $V^{(1)}(R)$. Thus we have

$$\frac{2A}{R^2}-\frac{B}{R}=0,\quad\text{for } R=R_{\rm eq}^{(0)}=\frac{2A}{B}\;,$$

but also

$$\frac{2A}{R^2}-\frac{B+C}{R}=0,\quad\text{for } R=R_{\rm eq}^{(0)}-\frac{2AC}{B^2}\;.$$

2. Systems with two characteristic lengths

If the system has more than one characteristic length, it may be possible by means of general principles to obtain more than one relationship satisfied by different components of the total energy E. For a neutral system of a finite number of point-charge bosons, for example, the quantum problem of determining the ground-state energy reduces in a certain approximation (Dyson, 1968) to the simple problem of determining the minimum of an expression of the form

$$\tilde{E}(\Lambda,\lambda)=\tilde{E}_l(\Lambda)+\tilde{E}_{mp}(\Lambda,\lambda)+\tilde{E}_q(\lambda)$$
$$\equiv(C_l/\Lambda^l)+(C_{mp}/\Lambda^m\lambda^p)+(C_q/\lambda^q)\ , \tag{3.21a}$$

where the C's and the l, m, p, and q are known constants, Λ is a measure of the linear dimension of the system, λ is a screening length, and Λ and λ are to be determined. [In the boson problem $\tilde{E}_l(\Lambda)$ and $\tilde{E}_{mp}(\Lambda,\lambda)$ are kinetic energies, while $\tilde{E}_q(\lambda)$ is a potential energy and $\lambda \ll \Lambda$, but these considerations need not here concern us.] The use of both

$$\partial\tilde{E}(\Lambda,\lambda)/\partial\Lambda=0 \tag{3.21b}$$

and

$$\partial\tilde{E}(\Lambda,\lambda)/\partial\lambda=0 \tag{3.21c}$$

gives us Λ and λ and therefore also the equilibrium value E of $\tilde{E}(\Lambda,\lambda)$. Of greater interest at the moment is that, proceeding precisely as for the one-characteristic-length case, Eq. (3.21b) gives

$$lE_l+mE_{mp}=0\ , \tag{3.22}$$

while Eq. (3.21c) gives

$$pE_{mp}+qE_q=0\ . \tag{3.23}$$

E_l, E_{mp}, and E_q are the equilibrium values of $\tilde{E}_l(\Lambda)$, $\tilde{E}_{mp}(\Lambda,\lambda)$, and $\tilde{E}_q(\lambda)$, respectively. (The fact that Λ and λ are ultimately related does not affect the derivation.) We have thereby by rather general procedures obtained *two* relationships satisfied by the components of E, with each relationship independent of the C's. The relationships will be exact if the *form* of $\tilde{E}(\Lambda,\lambda)$ is correct, even though the C's are surely not exact.

In the charged-boson problem just commented on, it turns out to be rather simple to obtain the forms of $\tilde{E}_l(\Lambda)$ and $\tilde{E}_q(\lambda)$ and, independently, two relationships satisfied by the three components of E, but rather difficult to obtain the form of $\tilde{E}_{mp}(\Lambda,\lambda)$. One could have worked backwards; knowing the two forms and the two relationships, one could easily have derived the form of $\tilde{E}_{mp}(\Lambda,\lambda)$. One further remark in this area may be interesting. The two relationships noted just above are the virial theorem for a finite number of bosons and the virial theorem for an infinite number of bosons; that these are different has already been observed—see Eqs. (3.14) and (3.19b). Given the two relationships, we can obtain the ratios E_l:E_{mp}:E_q immediately, without even knowing the forms of $\tilde{E}_l(\Lambda)$, $\tilde{E}_{mp}(\Lambda,\lambda)$, and $\tilde{E}_q(\lambda)$.

IV. MANY-ELECTRON ATOMS: SOME FORMALISM

A. A uniform number density *n*: a qualitative picture

1. Energies and radii

Many problems require much more information, such as energies of excitation, but it remains an interesting problem to estimate the total energy E of the ground state of a neutral heavy atom, with a nucleus of charge Ze. Furthermore, in the course of estimating E one obtains an estimate of the number density and therefore of the potential generated by the atom, and this can be useful for many problems. (Most of our considerations can be extended immediately to positive ions, but we shall temporarily restrict our attention to neutral atoms.) We assume that each electron (e^-) lies in one of a set of nonoverlapping small spheres of radius r_0; we thereby satisfy the Pauli principle. By the uncertainty principle, the kinetic energy of an individual e^- is then of order $p^2/m_e \approx \hbar^2/m_e r_0^2$, independent of the location of the small sphere. To maximize the magnitude of the potential energy, which will be seen shortly to be dominated by an attractive central potential, we distribute our small spheres uniformly within a large sphere of radius R, so that the number density $n(\mathbf{r})=n(r)$ is a constant within the large sphere and zero outside. Volume considerations give

$$Zr_0^3 \approx R^3\ , \tag{4.1}$$

and it follows that, for the ground state,

$$H(\mathbf{r}_1,\ldots,\mathbf{r}_Z,\mathbf{p}_1,\ldots,\mathbf{p}_Z)$$
$$=\sum_i[(p_i^2/2m_e)-(Ze^2/r_i)]+\tfrac{1}{2}e^2\sum_{i\neq j}\sum(1/r_{ij})$$
$$\approx Z(\hbar^2/m_e)(Z^{2/3}/R^2)-Z(Ze^2/R)+\tfrac{1}{2}Z^2e^2/R\ , \tag{4.2}$$

where we have set $p_i \approx \hbar/r_0 \approx Z^{1/3}\hbar/R$ and where we have approximated both $1/r_i$ and $1/r_{ij}$ by $1/R$. Actually, we are interested for the moment only in whether it is the attractive electron-nucleus or repulsive e^-e^- interaction which dominates. The attractive term dominates—if it did not, there would be neither atoms nor physicists—because of the factor of $\frac{1}{2}$ in the repulsive term and because, as follows from geometric considerations, the average value of $1/r_i$ is somewhat larger than the average value of $1/r_{ij}$. Having retained the schematic factor of 2 in the electron-electron term only to determine the overall sign of the potential-energy term, we now rewrite Eq. (4.2) as

$$H(\mathbf{r}_1,\ldots,\mathbf{p}_Z)\approx Z^{5/3}(\hbar^2/m_eR^2)-(Z^2e^2/R)$$
$$\equiv\tilde{E}_K(R)+\tilde{E}_V(R)\equiv\tilde{E}(R)\ . \tag{4.3}$$

Setting $d\tilde{E}/dR=0$ gives the equilibrium radius and then substituting back into $\tilde{E}(R)$ gives two of the most significant results obtained from TF theory (but TF theory gives much more accurate numerical coefficients), namely,

$$R(\text{atom})\approx a_0/Z^{1/3} \quad \text{and} \quad E(\text{atom})\approx -Z^{7/3}(e^2/a_0)\ . \tag{4.4}$$

The Z dependences are the interesting results, the a_0 and e^2/a_0 factors following, as for the H atom, from dimensional arguments. It is important to recognize that the forms of R(atom) and of E(atom) would in no way be changed if there were no electron-electron interaction

[Attractive interactions are not merely stronger than the repulsive ones, with the factor 2 playing an important role, but in a sense are almost completely dominant; thus it will be seen later that for a neutral atom of large Z their contribution to the total energy of the atom is seven times greater. This is the underlying reason that a central-field approximation can provide good results. The origin of the factor of 2 might therefore be worth noting; no such factor appears, for example, in a neutral plasma of protons and electrons. In the atomic case of present interest, there are Z attractive interactions, each of strength $-Ze^2$, giving rise to the $-Z^2e^2$ factor, and $Z^2/2$ repulsive e^-e^- interactions, each of strength e^2, generating the $+(Z^2e^2)/2$ factor; there are *also* $Z^2/2$ repulsive (Coulomb) proton-proton interactions, each of strength e^2, within the nucleus, but in the present context these are irrelevant, having been absorbed in the definition of the zero-energy reference level.]

One immediate objection to the above approach is that the Pauli principle was satisfied in an unnecessarily restrictive fashion; wave functions need not be nonoverlapping in order to be orthogonal. That this is not a problem, within the limited accuracy we seek, is suggested by considering N noninteracting fermions moving in the one-dimensional region $0\leq x\leq L$. To simplify the discussion we assume that all of the fermions have the same spin projection. For the true ground state, the fermions have overlapping wave functions, with the ith fermion having a wavelength $2L/i$, and we find for the ground-state energy

$$E(L)=\frac{h^2}{8mL^2}\sum_{i=1}^{N} i^2 \approx \frac{N^3h^2}{24mL^2}\ .$$

In the last step we assumed that $N\gg 1$. If, in analogy to placing each electron in its own sphere, we place each fermion in its own strip, of length L/N, with each fermion having a wavelength $2L/N$, the approximate ground-state energy is readily found to be $3E(L)$. The error is therefore merely a factor of order unity, independent of N. [The lowered energy associated with the better (overlapping) wave functions can play the crucial role in some areas, for example in the formation of solids, but that need not here concern us.] It is simple to see why the error is of order unity. The wavelength of the ith state is $\lambda_i=2L/i$ in the exact formulation, and $\tilde{\lambda}_i=2L/N$ in the approximate formulation, where $1\leq i\leq N$. It follows that $\tilde{\lambda}_i$ is very different from λ_i for $i\ll N$, but that $\lambda_i\approx\tilde{\lambda}_i$ for $i\approx N$, and the sum of the kinetic energies is strongly dominated by the particles with very small wavelengths.

In our estimation of $\tilde{E}(R)$, in Eq. (4.3), we ignored the fact that *two* electrons (with spins up and down) could be placed in each small sphere, for we are not here normally concerned with "mere" factors of 2, but it is of interest to consider the general case of fermions of spin S with associated multiplicity $q\equiv 2S+1$. We can then place q fermions in each of Z/q small spheres, and volume considerations now give $(Z/q)r_0^3\approx R^3$ rather than Eq. (4.1), which might indeed have been written $(Z/2)r_0^3\approx R^3$. The expression for $\tilde{E}_K(R)$ in Eq. (4.3) therefore becomes

$$\tilde{E}_K(R)\approx q^{-2/3}Z^{5/3}(\hbar^2/m_eR^2)\ , \tag{4.5}$$

and Eq. (4.4) is replaced by

$$R\approx a_0/(q^{2/3}Z^{1/3}),\quad E\approx -Z^{7/3}q^{2/3}(e^2/a_0)\ . \tag{4.6}$$

The choice $q=Z$ allows as many projections as there are fermions, and the analysis, developed for fermions, is applicable to bosons. For $q=Z$, Eq. (4.6) gives, for an "atom" consisting of a heavy nucleus of charge Ze and Z bosons of charge $-e$ and mass m_e,

$$\begin{aligned} &R(\text{“atom,” bosons})\approx a_0/Z\ ,\\ &E(\text{“atom,” bosons})\approx -Z^3(e^2/a_0)\ , \end{aligned} \tag{4.7}$$

as expected, since each of the Z bosons can occupy a K-shell orbital. These results emphasize the well-known fact that the fermion character of electrons greatly increases the size and greatly raises the energy of atoms (and ultimately of matter) over the values that would follow from quantum mechanics without a Pauli exclusion principle. (Indeed, as noted earlier, Dyson has shown that matter would collapse if there were no exclusion principle.)

Some of the results just obtained may seem obvious. If so, that might be more a consequence of familiarity than of logic. Thus, for example, it had long been generally believed that it was primarily the Coulomb repulsion between electrons which prevented the formation of stable highly negative ions, but in fact the formation of such negative ions for "bosonic electrons" is quite possible. It is the Pauli principle that plays the dominant role in preventing highly negative ions from being stable (see Benguria and Lieb, 1983). Even those of us with a kinship for physical arguments and a distaste for epsilonics must occasionally recognize that hand-waving has its limitations.

2. Conditions for collapse

We discuss the collapse of a heavy neutral atom in Sec. III.B.2. We shall here again discuss that question, but in the rougher ultrarelativistic approximation, using the qualitative picture for a uniform number density just discussed. Thus we replace $\sum_i (p_i^2/2m_e)$ in H of Eq. (4.2) by $\sum_i p_i c$ and once again use $p_i \approx Z^{1/3}\hbar/R$. Equation (4.3) is then replaced by

$$H(\text{ultra};\mathbf{r}_1,\ldots,\mathbf{p}_Z)=(Z^{4/3}\hbar c - Z^2 e^2)/R \ .$$

The condition for collapse is therefore

$$Z^{2/3}(e^2/\hbar c)=Z^{2/3}\alpha \geq 1 \ ,$$

in good agreement with the result obtained in Sec. III.B.2 using a less brutal approximation.

B. A variable number density $n(r)$

1. The Lenz energy functional

We can readily drop the overly simplifying assumption that $n(\mathbf{r})$ is a constant, $n \approx Z/R^3$, for $r<R$ and is zero for $r>R$. (This generalization to a variable density will enable us to concentrate the electrons near the origin, with the increase in kinetic energy and electron-electron repulsion more than compensated for by the increase in electron-nucleus attraction.) Under that assumption the kinetic energy per unit volume in the inner region was, using the expression for $\widetilde{E}_K(R)$ in Eq. (4.3),

$$\widetilde{E}_K(R)/\text{Vol} \approx (\hbar^2/m_e)(Z^{5/3}/R^5) \approx (\hbar^2/m_e)n^{5/3} \ . \tag{4.8}$$

If the kinetic energy per unit volume is slowly varying, an adequate expression for $\widetilde{E}_K(R)$ would therefore be the integral over all coordinate space of the right-hand side of Eq. (4.8), with n replaced by $n(\mathbf{r})$. Inserting the correct numerical coefficient k—we shall return to this point shortly—we obtain the ground-state energy of an atom or ion within the TF model as a functional of n, with n now a function of $\mathbf{r}$,

$$\widetilde{E}[n]=\widetilde{E}_K[n]+\widetilde{E}_{ev}[n]+\widetilde{E}_{ee}[n] \ , \tag{4.9a}$$

where

$$\widetilde{E}_K[n]=k(\hbar^2/m_e)\int n^{5/3}(\mathbf{r})d\mathbf{r} \ , \tag{4.9b}$$

$$\widetilde{E}_{ev}[n]=-Ze^2\int \frac{n(\mathbf{r})}{r}d\mathbf{r} \ , \tag{4.9c}$$

$$\widetilde{E}_{ee}[n]=\frac{e^2}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' \ , \tag{4.9d}$$

$$\int n(\mathbf{r})d\mathbf{r}=N \ , \tag{4.9e}$$

$$n(\mathbf{r})\geq 0 \ , \tag{4.9f}$$

and

$$k \equiv (3\pi^2/10)(3/\pi)^{2/3} \ . \tag{4.9g}$$

[Though we had been concerned with neutral atoms, Eq. (4.9) is valid also for ions. It was only necessary to impose a normalization condition, Eq. (4.9e), in which the number of electrons is N, with N arbitrary. We shall see later that TF theory says little for $N>Z$, but, though the results obtained do not scale as they do for $N=Z$, TF theory is useful for $N<Z$. The Z that appears in Eq. (4.9c) defines the nuclear charge, not the number of electrons, and therefore remains unchanged.] Note that Eq. (4.9) does not contain any element of discreteness, no sum appearing. N need therefore no longer be thought of as an integer—the number of electrons—but can be taken to be continuous. Z can of course also be taken to be continuous. The TF model energy functional was first obtained by Lenz (1932).

(Note that for n spherically symmetric and for $N \leq Z$, a case discussed below, $1/|\mathbf{r}-\mathbf{r}'| \rightarrow 1/r_> \leq 1/r$, and $\widetilde{E}_{ee}[n] \leq -(N/2Z)\widetilde{E}_{ev}[n] \leq \frac{1}{2}|\widetilde{E}_{ev}[n]|$, as for the simpler model discussed above.)

To obtain the value of k given by Eq. (4.9g), we recall that two electrons can be accommodated in a volume of phase space $d\mathbf{r}\,d\mathbf{p}$ equal to h^3. It follows that the TF kinetic-energy functional is

$$\widetilde{E}_K[n]=\int\int{}' 2\frac{d\mathbf{r}\,d\mathbf{p}}{h^3}\frac{p^2}{2m_e} \ . \tag{4.10}$$

The prime on the integral denotes the fact that for a given $\mathbf{r}$ the upper limit on p is the Fermi momentum $p_F(r)$, defined by

$$2(4\pi/3)p_F^3(\mathbf{r})/h^3=n(\mathbf{r}) \ . \tag{4.11}$$

In arriving at Eq. (4.11) we again recognized that two electrons can be accommodated in a volume of phase space equal to h^3. Integration over $\mathbf{p}$ in Eq. (4.10) and the use of Eq. (4.11) gives Eq. (4.9b), with k defined by Eq. (4.9g).

2. Derivation of the Thomas-Fermi differential equation from the Lenz energy functional

We seek the lowest energy for the $\widetilde{E}[n]$ defined by Eq. (4.9). (In the course of doing so, we hope to clarify some of the brief comments made in the subsection "Remarks" in Sec. I.) We demand that the variation $\delta\widetilde{E}[n]$ of $\widetilde{E}[n]$ satisfy $\delta\widetilde{E}[n]\geq 0$. We *cannot* demand stationarity, that is, $\delta\widetilde{E}[n]=0$; there is no physical or mathematical basis for making such a demand. (It should be made perfectly clear to the reader that the author has not suddenly developed an interest in rigor or completeness, nor has he become pedantic. Rather, there are important cases in which there are nonvanishing *first-order* corrections to $\widetilde{E}[n]$ in the neighborhood of the $n(\mathbf{r})$ that minimizes $\widetilde{E}[n]$. The positive ion, to be discussed briefly in Sec. V, is one such example. A second example, which involves a modified form of $\widetilde{E}[n]$ and which will be considered in some detail in the present section and in Sec. V, is a simple model of an atom in which the electron-electron interaction is turned off; the appropriate $\widetilde{E}[n]$ is then obtained from Eq. (4.9) by simply dropping the $\widetilde{E}_{ee}[n]$ term.) Now we can find the stationary values or the extremum values—the latter need not be stationary; $f(x)=|x|$ is not stationary at its minimum at $x=0$—of a function, subject to constraints, by means of one Lagrange multiplier for each constraint. The same is true of functionals. In particular, we seek the minimum value of $\tilde{E}[n]$, defined by Eqs. (4.9a)–(4.9d) and (4.9g), subject to the normalization constraint, Eq. (4.9e), and to the constraint defined by Eq. (4.9f), namely, $n(\mathbf{r}) \geq 0$. To incorporate the normalization constraint, we introduce the functional

$$F[n] \equiv \tilde{E}[n] + \mu \left[\int n(\mathbf{r}) d\mathbf{r} - N \right]$$

with μ a Lagrange multiplier. We *cannot* demand that $\delta F[n]$ vanish; rather, we demand that

$$\delta F[n] \geq 0 \ ,$$

subject to the restriction $n(\mathbf{r}) \geq 0$. We must consider the possibility that $n(\mathbf{r})=0$ over some three-dimensional region, not simply at the point at infinity. [This may not seem "natural," since, as noted above, for a real atom or ion, and indeed for any quantum-mechanical problem, the number density vanishes over an extended region if and only if the potential is positive and infinite over that region. In the Schrödinger equation with a nonsingular potential, for example, a wave function that vanished over a region would vanish everywhere. In the TF differential equation, $n(\mathbf{r})$ appears to the two-thirds power, so that derivatives of $n(\mathbf{r})$ are singular for $n(\mathbf{r})=0$, and $n(\mathbf{r})$ can vanish identically in a region and yet not vanish everywhere. The crucial point is not simply the nonlinearity of the TF differential equation, but the appearance of a fractional power. We shall consider the nature of the singularity—when there is a singularity—in Sec. V.B.3. The possibility that $n(\mathbf{r})$ can vanish over a three-dimensional region including the point at infinity can perhaps best be understood by recalling that TF theory is semiclassical, and that in a classical theory the space available to a particle with energy below zero is limited. In a positive ion, the energy of the least-bound electron, which is nothing other than ϵ_F, lies below zero. We therefore expect to find, and do find, that $n(\mathbf{r})=0$ over a three-dimensional region. For a neutral atom, on the other hand, the energy of the least-bound electron in TF theory is vanishingly small, that is, $\epsilon_F=0$, and $n(\mathbf{r})$ should not be expected to be identically zero except at infinity. In Sec. V.C, where we consider a quantum-mechanically solvable model of the atom in which there is no electron-electron interaction, we show that, not surprisingly, the radius of the sphere beyond which $n(r)=0$ in TF theory follows precisely from a study of the WKB approximation to the exact wave functions.] We now have

$$\delta F = \int \left[\frac{5}{3} k \frac{\hbar^2}{m_e} n^{2/3}(\mathbf{r}) - \frac{Ze^2}{r} + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu \right] \delta n(\mathbf{r}) d\mathbf{r} \geq 0 \ . \tag{4.12}$$

Where $n(\mathbf{r})>0$, the (infinitesimal) variation $\delta n(\mathbf{r})$ of $n(\mathbf{r})$ is arbitrary, and the quantity in large parentheses in Eq. (4.12) must vanish identically. If it did not, one would find a subregion in which the term in large parentheses was of definite sign, one could choose $\delta n(\mathbf{r})$ to be of opposite sign in that subregion and zero elsewhere, and one would have $\delta F<0$, in violation of the requirement. Thus, where $n(\mathbf{r})>0$, the requirement $\delta F \geq 0$ is equivalent to the requirement $\delta F=0$, requiring the coefficient of $\delta n(\mathbf{r})$ to vanish, as is usual in the calculus of variations. We therefore have

$$\frac{5}{3} k \frac{\hbar^2}{m_e} n^{2/3}(\mathbf{r}) - \frac{Ze^2}{r} + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu = 0 \tag{4.13a}$$

for $\mathbf{r}$ in the region where $n(\mathbf{r})>0$. If, however, there is a three-dimensional region in which $n(\mathbf{r})=0$, then $\delta n(\mathbf{r})$ is *not* arbitrary in that region; since any trial number density is to be positive, it follows that $\delta n(\mathbf{r}) \geq 0$ when $n(\mathbf{r})=0$. The restriction on the term in large parentheses in Eq. (4.12) can then be relaxed; it need not vanish, but need only be non-negative. Further, the $n^{2/3}$ term vanishes. We thereby arrive at

$$-\frac{Ze^2}{r} + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \mu \geq 0 \tag{4.13b}$$

for $\mathbf{r}$ in the region where $n(\mathbf{r})=0$. By Eqs. (4.9g) and (4.11), the first term in Eq. (4.13a) can be rewritten as

$$(5/3)k(\hbar^2/m_e)n^{2/3}(\mathbf{r}) = p_F^2(\mathbf{r})/2m_e \ . \tag{4.14}$$

Furthermore, the potential energy of an electron at the point $\mathbf{r}$ is, in the TF approximation,

$$V(\mathbf{r}) = -\frac{Ze^2}{r} + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \ . \tag{4.15}$$

[Note again that $n(\mathbf{r}')$ contains a contribution from the electron whose potential energy is being determined. This defect of the TF approximation will have little effect on the ground-state energy of the atom or ion for $N \leq Z$ and N sufficiently large. For $N>Z$ the defect is of great importance, being a primary reason why the TF approximation cannot account for negative ions. Thus, as noted in Sec. I, in lowest approximation the effective potential seen by the outermost electron, for $N=Z+1$, does not fall off asymptotically as an attractive r^{-4} polarization potential, as for a real atom. The r^{-4} term exists but is not the dominant term; the effective potential is repulsive and is given asymptotically by e^2/r. As discussed in Sec. V.B.2, this defect is also responsible for the zero value of ϵ_F for a neutral atom in TF theory.] We can therefore write Eqs. (4.13a) and (4.13b) as

$$p_F^2(\mathbf{r})/2m_e + V(\mathbf{r}) = \epsilon_F \ , \tag{4.16a}$$

for $\mathbf{r}$ in the region where $n(\mathbf{r})>0$, and

$$V(\mathbf{r}) \geq \epsilon_F \ , \tag{4.16b}$$

for $\mathbf{r}$ in the region where $n(\mathbf{r})=0$, where we have written

$$\mu=-\epsilon_F \ , \tag{4.17}$$

with ϵ_F the Fermi energy. We must have

$$\epsilon_F \le 0 \ . \tag{4.18}$$

This follows from Eq. (4.16b) under the reasonable assumption that $n(\infty)=V(\infty)=0$. [It is simple enough to prove Eq. (4.18) without that assumption.] Operating on Eq. (4.15) with the Laplacian gives the Poisson equation

$$\nabla^2 V(\mathbf{r})=4\pi Ze^2\delta(\mathbf{r})-4\pi e^2 n(\mathbf{r}) \ , \tag{4.19}$$

with $\delta(\mathbf{r})$ a Dirac delta function. Operating on Eq. (4.13a) with ∇^2 gives

$$(5/3)k(\hbar^2/m_e)\nabla^2 n^{2/3}(\mathbf{r})+4\pi e^2[Z\delta(\mathbf{r})-n(\mathbf{r})]=0 \ , \tag{4.20}$$

for $\mathbf{r}$ in the region where $n(\mathbf{r})>0$. We have not proved it—it is not hard to do so—but it is physically clear that the region defined by $n(\mathbf{r})=0$ does not include the origin. If then we operate on Eq. (4.13b) with ∇^2, we obtain the trivial result that $n(\mathbf{r})\le 0$ where $n(\mathbf{r})=0$.

The condition on $n(\mathbf{r})$ arrived at above is a consequence of having demanded that $\delta\tilde{E}[n]\ge 0$. There is therefore no guarantee that the condition on $n(\mathbf{r})$, given by Eq. (4.20), leads to the minimum value of $\tilde{E}[n]$. With $\delta\tilde{E}[n]$ and $\delta^2\tilde{E}[n]$ the first- and second-order variations of $\tilde{E}[n]$, the possibilities to be considered include the following:

(α) $\delta\tilde{E}[n]>0$: $\tilde{E}[n]$ has a minimum that is nonstationary, that is, a minimum with a cusp at the $n(\mathbf{r})$ defined by Eq. (4.20).

(β) $\delta\tilde{E}[n]=0$ and $\delta^2\tilde{E}[n]<0$: $\tilde{E}[n]$ has a local maximum at the $n(\mathbf{r})$ defined by Eq. (4.20).

(γ) $\delta\tilde{E}[n]=0$ and $\delta^2\tilde{E}[n]>0$: $\tilde{E}[n]$ has a local minimum at the $n(\mathbf{r})$ defined by Eq. (4.20). (Note: $\delta\tilde{E}[n]=0$ implies that there is no first-order error. $\delta\tilde{E}[n]>0$ implies that, for any $n(\mathbf{r})$ other than that defined by Eq. (4.20), there is a first-order error.)

We shall not consider the possibility that $\delta\tilde{E}[n]$ and $\delta^2\tilde{E}[n]$ both vanish.

We show in Appendix A that $\tilde{E}[n_t]>\tilde{E}[n]$ for any normalized $n_t(\mathbf{r})$ different from the $n(\mathbf{r})$ defined by Eq. (4.20). Here, we limit our considerations to a proof that $\tilde{E}[n]$ is at least a *local* minimum, that is, that $\tilde{E}[n+\delta n]>\tilde{E}[n]$, where $n(\mathbf{r})+\delta n(\mathbf{r})$ is normalized. For case (α), with $\delta\tilde{E}[n]>0$, this is immediately true. If $\delta\tilde{E}[n]=0$, we must show that $\delta^2\tilde{E}[n]>0$. By Eq. (4.9), we have

$$\delta^2\tilde{E}[n]=(1/2)(5/3)(2/3)k(\hbar^2/m_e) \times\int n^{-1/3}(\mathbf{r})[\delta n(\mathbf{r})]^2 d\mathbf{r}+S[\delta n] \ ,$$

where

$$S[\delta n]\equiv\frac{e^2}{2}\int\int\frac{\delta n(\mathbf{r})\delta n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' \ .$$

The first term in $\delta^2\tilde{E}[n]$ is clearly non-negative since $n(\mathbf{r})\ge 0$. We can show that S is also non-negative using a mathematical or physical argument. Thus, mathematically, since

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|}=\frac{1}{2\pi^2}\int\frac{e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}}{q^2}d\mathbf{q} \ ,$$

we can write

$$S[\delta n]=\frac{e^2}{2}\cdot\frac{1}{2\pi^2}\int\frac{d\mathbf{q}}{q^2}\left|\int e^{i\mathbf{q}\cdot\mathbf{r}}\delta n(\mathbf{r})d\mathbf{r}\right|^2\ge 0 \ .$$

Physically, S represents the self-energy of a charge distribution $\delta n(\mathbf{r})$, where $\delta n(\mathbf{r})$ need not be of one sign, and self-energies are non-negative. (The self-energy S can readily be cast into the form of an integral over the square of the electric field, with a positive coefficient, so that we surely have $S\ge 0$.) Finally, we do indeed have $\delta^2\tilde{E}[n]\ge 0$. This establishes the local-minimum property of $\tilde{E}[n]$ for the $n(\mathbf{r})$ defined above.

We note that we can eliminate any two of the three variables $n(\mathbf{r})$,$p_F(\mathbf{r})$, and $V(\mathbf{r})$, related by Eqs. (4.14), (4.16), and (4.19). The differential equation satisfied by $n(\mathbf{r})$ has already been given, in Eq. (4.20). It will be useful to record also the differential equation for $V(\mathbf{r})$, which follows from Eqs. (4.19), (4.11), and (4.16) and is given by

$$\nabla^2 V(\mathbf{r})=4\pi Ze^2\delta(\mathbf{r})-\frac{4e^2}{3\pi}\left[\frac{2[\epsilon_F-V(\mathbf{r})]}{e^2 a_0}\right]^{3/2} \ , \quad V(\mathbf{r})<\epsilon_F \ , \tag{4.21a}$$

$$\nabla^2 V(\mathbf{r})=0, \quad V(\mathbf{r})\ge\epsilon_F \ . \tag{4.21b}$$

We shall obtain a simplified version of Eq. (4.21) in Sec. V. We can readily invert Eqs. (4.20) and (4.21) and obtain integral equations for $n(\mathbf{r})$ and $V(\mathbf{r})$, respectively. For the neutral atom, the integral equation for $n(\mathbf{r})$ is

$$n(\mathbf{r})=\frac{1}{3\pi^2}\left[\frac{2}{a_0}\right]^{3/2}\left[\frac{Z}{r}-\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\right]^{3/2} \ .$$

For the spherically symmetric case, this reduces to

$$n(r)=\frac{16}{3}\left[\frac{2}{\pi a_0^3}\right]^{1/2}\left[\int_r^\infty n(r')\left[\frac{1}{r}-\frac{1}{r'}\right](r')^2 dr'\right]^{3/2} \ . \tag{4.22}$$

There is an alternative to a direct numerical solution of Eq. (4.20) or Eq. (4.21). Since Eq. (4.21) follows from the minimization of $\tilde{E}[n]$ as given by Eq. (4.9), we can assume a particular form for $n(\mathbf{r})$, one that contains one or more variational parameters c_p and that allows one to perform the integrations in Eq. (4.9) analytically; one then varies the c_p to minimize the energy. In general, this procedure introduces a *first-order* error in $\delta n(\mathbf{r})$. If, however, $n(\mathbf{r})>0$ for all $\mathbf{r}$ but the point at infinity, which will be seen to be the case for the neutral atom, for example, the error is of second order in $\delta n(\mathbf{r})$, that is, the procedure is a variational one.

3. Direct derivation of the Thomas-Fermi differential equation

The TF differential equation (4.21) was seen to follow from Eqs. (4.14), (4.16), and (4.19). We can simply write down two of the three equations: Eq. (4.19) is the Poisson equation, while Eq. (4.14) gives $n(\mathbf{r})$ in terms of the available volume in phase space. The third equation, Eq. (4.16), was obtained by varying the Lenz energy functional. It will be interesting to derive Eq. (4.16) directly. We define $\epsilon_F(\mathbf{r})$ by the relation

$$\epsilon_F(\mathbf{r})=p_F^2(\mathbf{r})/(2m_e)+V(\mathbf{r}) .$$

As noted in the Introduction, it is often asserted, on (false) physical grounds, that $\epsilon_F(\mathbf{r})=0$, but in general that is not true. The error is associated with the natural but incorrect assumption, discussed above, that $n(\mathbf{r})$ can vanish only at infinity.

To begin, consider the region where $n(\mathbf{r})>0$. If $\epsilon_F(\mathbf{r})$ were not a constant in that region, one could lower the energy of the system by moving an electron from the top of the Fermi sea at any point where $\epsilon_F(\mathbf{r})$ did not assume its minimum value to just above the top of the Fermi sea at a point where $\epsilon_F(\mathbf{r})$ was lower. But one cannot lower the energy of the system when it is in its lowest state. It follows that $\epsilon_F(\mathbf{r})=\text{const}\equiv\epsilon_R$ where $n(\mathbf{r})>0$, that is,

$$p_F^2(\mathbf{r})/(2m_e)+V(\mathbf{r})=\epsilon_F, \quad \text{where } n(\mathbf{r})>0 .$$

Now consider the region, if such a region exists, where $n(\mathbf{r})=0$. Since there are no electrons to move around in that region, there need be no contradiction if $\epsilon_F(\mathbf{r})$ is not constant in that region. There *will* be a contradiction if $\epsilon_F(\mathbf{r})$ at any point in the region where $n(\mathbf{r})=0$ lies below ϵ_F, for then the energy of the system could be lowered by moving an electron from the top of the Fermi sea with an energy ϵ_F, in the region where there are electrons, to the point where $n(\mathbf{r})=0$ and where the energy lies below ϵ_F. Since $p_F(\mathbf{r})=0$ where $n(\mathbf{r})=0$, the energy in that region is simply $V(\mathbf{r})$. We therefore conclude that we must have

$$\epsilon_F\le V(\mathbf{r}), \quad \text{where } n(\mathbf{r})=0 .$$

These last two equations are identical to Eq. (4.16) obtained earlier from the Lenz energy functional.

Note that if the system is in its ground state and an electron in the region where $n(\mathbf{r})>0$, with an energy ϵ_F, is moved to a point $\mathbf{r}'$ in the region where $n(\mathbf{r}')=0$ and where $V(\mathbf{r}')>\epsilon_F$, the change in energy will not be of second order but will be the *first-order* term $\epsilon_F-V(\mathbf{r}')$; $\mathbf{E}[n]$ for n in the neighborhood of the minimizing distribution is *not* stationary, and in seeking the minimizing distribution we can demand that $\delta\tilde{E}[n]\ge0$ but we *cannot* demand that $\delta\tilde{E}[n]=0$. We can restate the above remark in terms of surfaces. The surface $\tilde{E}[n]$ in the neighborhood of the minimizing number density is horizontal for variations of $n(\mathbf{r})$ that represent the movement of charge between two points at which there are electrons, but the surface has a discontinuous derivative for variations of $n(\mathbf{r})$ that represent the movement of charge from a point where there are electrons to a point where (initially) there are not.

We replaced the Lagrange multiplier μ, used in the minimization of the energy to account for the constraint on the number N of electrons, by $-\epsilon_F$. The concept of the Fermi energy, the energy of the least-bound electron, is a very useful concept, one we have already used, but we have justified our identification of μ with $-\epsilon_F$ only for the $\tilde{E}[n]$ defined by Eq. (4.9). We now justify that identification for the more general form of the energy functional,

$$\tilde{E}[n]=\int K(n)d\mathbf{r} ,$$

with the energy density $K(n)$ arbitrary. [It is very useful these days to consider the more general case, for whereas $n(\mathbf{r})$ had long been assumed to be a useful but not basic construct, less fundamental than the wave function because it does not contain phase information, one now knows from the work of Hohenberg and Kohn (1964) that the ground-state energy is uniquely defined by $n(\mathbf{r})$.] We then have, for arbitrary $n(\mathbf{r})$, and for N large enough to be considered continuous,

$$\frac{d\tilde{E}}{dN}=\int\frac{dK}{dn}\frac{dn}{dN}d\mathbf{r} .$$

To obtain the $n(\mathbf{r})$ which, for *fixed N*, minimizes the energy, we minimize

$$F[n]\equiv\int K(n)d\mathbf{r}+\mu\left[\int n(\mathbf{r})d\mathbf{r}-N\right]$$

with respect to variations in n and arrive at

$$\mu=-\frac{dK}{dn} .$$

We therefore have, with $\tilde{E}$ reducing to E for n the minimizing n,

$$\frac{dE}{dN}=-\mu\int\frac{dn}{dN}d\mathbf{r}=-\mu\frac{d}{dN}\int n(\mathbf{r})d\mathbf{r}$$
$$=-\mu\frac{d}{dN}N=-\mu .$$

Since $N\gg1$, it follows that dE/dN, and therefore $-\mu$, is the change in energy on adding one electron, which by definition is ϵ_F.

V. REAL AND MODEL MANY-ELECTRON ATOMS: SOME RESULTS

A. Noninteracting fermions in a one-dimensional interval

Before turning to real and model atoms, we consider the problem of the determination of the ground-state energy $E(L)$ of N noninteracting fermions moving in the one-dimensional interval $0 \leq x \leq L$, where, to simplify the discussion, we assume that all of the fermions have the same spin projection. We considered this problem in Sec. IV.A, where we solved it both exactly—more precisely, we obtained the leading term of the exact solution—and in the approximation in which the fermions were in nonoverlapping strips, to see the effect of implementing the Pauli principle in the somewhat crude but simple way. We are now interested in the accuracy of the TF approximation, and we therefore solve the same problem in the TF approximation, and exactly.

The fermions have only kinetic energy, and we must therefore have $p_F(x) = \text{const} = p_F$, for otherwise we could move fermions around and lower the energy of the system. The value of p_F follows from the normalization condition

$$N = \int_0^L \int_{-p_F}^{p_F} dx\, dp_x/h = 2Lp_F/h \ ,$$

with $dx\, dp_x/h$ the one-dimensional analog of $d\mathbf{r}\, d\mathbf{p}/h^3$. We then have, as the TF approximation to $E(L)$,

$$\begin{aligned} E_{TF}(L) &= \int_0^L \int_{-p_F}^{p_F} (dx\, dp_x/h)(p_x^2/2m) \\ &= Lp_F^3/3mh = N^3h^2/24mL^2 \ . \end{aligned}$$

The exact answer, since the ith wavelength is $\lambda_i = 2L/i$, is

$$\begin{aligned} E(L) &= \frac{h^2}{2m} \sum_{i=1}^{N} \frac{1}{\lambda_i^2} \\ &= \frac{h^2}{8mL^2} \sum_{i=1}^{N} i^2 \\ &= \frac{N^3h^2}{24mL^2} \left[1 + \frac{3}{2N} + \frac{1}{2N^2} \right] \ . \end{aligned}$$

It follows that

(α) the TF approximation gives the leading term *exactly,* and

(β) the relative error is of the order of $1/N$.

We also note that $\epsilon_F = p_F^2/2m = N^2h^2/(8mL^2)$ is exactly the same as the energy of the most energetic state occupied by a fermion. Further, the uniform density N/L predicted by TF theory agrees to lowest order, other than for $x \simeq 0$ and $x \simeq L$, with the exact density, which is simple to evaluate since the ith wave function has the form $(2/L)^{1/2}\sin(i\pi x/L)$. (In the true problem the probability of finding a fermion at $x=0$ or L, where the wave function must vanish, is zero; to preserve normalization, the probability of finding an electron in the real problem at points other than in the immediate region of $x=0$ or L must, on average, be slightly enhanced relative to the uniform distribution for the probability obtained in our TF approximation.)

It is simple to check that the above remarks are not restricted to the one-dimensional case but remain valid for noninteracting fermions in a cube.

B. Real atoms

1. Spherical symmetry

It would be possible to add to the two restrictions built into Eq. (4.9) a third, on the angular momentum, and to seek the lowest energy for a given angular momentum. Not having built in such a restriction, we might expect that in the TF approximation the state of lowest energy will be spherically symmetric for all values of Z. We shall now show this to be the case. [Those who find the result we are about to prove physically obvious can skip ahead to the paragraph containing Eq. (5.3).] To begin, we decompose $n(\mathbf{r})$ into its spherically symmetric component $n_0(r)$, and the spherically asymmetric residue $n_1(\mathbf{r})$. Thus we write

$$n(\mathbf{r}) = n_0(r) + n_1(\mathbf{r}) \ , \tag{5.1a}$$

where

$$n_0(r) \equiv (1/4\pi) \int n(\mathbf{r})\, d\Omega_{\hat{r}} \geq 0 \ , \tag{5.1b}$$

where $d\Omega_{\hat{r}}$ is the differential solid angle associated with $\mathbf{r}$, and the inequality in (5.1b) is a consequence of the inequality $n(\mathbf{r}) \geq 0$. It follows from Eqs. (5.1a) and (5.1b) that

$$\int n_1(\mathbf{r})\, d\Omega_{\hat{r}} = 0 \ . \tag{5.2}$$

This result is in any event obvious since, by construction, $n_1(\mathbf{r})$ has no zero-angular-momentum component. Inserting $n(\mathbf{r})$ given by Eq. (5.1a) into Eq. (4.9) for $\tilde{E}[n]$, we use Eq. (5.2) to eliminate a term in $\tilde{E}_{ev}[n]$ linear in $n_1(\mathbf{r})$, and we use the fact that $|\mathbf{r}-\mathbf{r}'|^{-1}$ cannot connect n_0 terms (with angular momentum zero) to n_1 terms (with angular momentum other than zero) to eliminate the $n_0(r)n_1(\mathbf{r}')$ and $n_1(\mathbf{r})n_0(r')$ terms in $\tilde{E}_{ee}[n]$. We thereby obtain

$$\tilde{E}[n] = \tilde{E}[n_0] + (k\hbar^2/m_e)M + S[n_1] \ ,$$

where

$$M \equiv \int [n^{5/3}(\mathbf{r}) - n_0^{5/3}(r)]\, d\mathbf{r} \ ,$$

$$S[n_1] \equiv \frac{e^2}{2} \int \int \frac{n_1(\mathbf{r})n_1(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' \ .$$

The proof that $S[n_1] > 0$ is identical to the proof used in Sec. IV, in the course of proving that $\delta^2\tilde{E}[n] \geq 0$, to show that $S[\delta n] \geq 0$. Turning to M, we write

$$\begin{aligned} \int n_0^{5/3}(r)\, d\mathbf{r} &= \int n_0(r) n_0^{2/3}(r)\, d\mathbf{r} \\ &= \int [n(\mathbf{r}) - n_1(\mathbf{r})] n_0^{2/3}(r)\, d\mathbf{r} \\ &= \int n(\mathbf{r}) n_0^{2/3}(r)\, d\mathbf{r} \ , \end{aligned}$$

using Eq. (5.2) in the last step. With the identifications $x = \mathbf{r}$, $p = 5/3$, $q = 5/2$, $f(\mathbf{r}) = n(\mathbf{r})$, and $g(\mathbf{r}) = n_0^{2/3}(r)$, the Hölder inequality given below Eq. (3.9) yields, when applied to the equation just above,

$$\int n_0^{5/3}(r)d\mathbf{r} \le \left[\int n^{5/3}(\mathbf{r})d\mathbf{r}\right]^{3/5}\left[\int n_0^{5/3}(r)d\mathbf{r}\right]^{2/5} ,$$

or

$$\int n_0^{5/3}(r)d\mathbf{r} \le \int n^{5/3}(\mathbf{r})d\mathbf{r} ,$$

or $M \ge 0$ and therefore, finally,

$$\tilde{E}[n] \ge \tilde{E}[n_0] .$$

In other words, the addition of an element of spherical asymmetry will necessarily increase the energy of the system. {Note that the proof that $\tilde{E}[n] \ge \tilde{E}[n_0]$ does *not* require n_0 to be the minimizing number density; for $\tilde{E}[n]$ defined by Eqs. (4.9a)–(4.9d), and (4.9g), the inequality is satisfied for any normalized $n_0(\mathbf{r}) = n_0(r)$ and any normalized $n(\mathbf{r}) = n_0(r) + n_1(\mathbf{r})$.} The proof is valid for atoms and ions.

We therefore have $p_F(\mathbf{r}) = p_F(r)$, $n(\mathbf{r}) = n(r)$, and $V(\mathbf{r}) = V(\mathbf{r})$. We now define $\phi(x)$ by means of

$$V(r) - \epsilon_F = -(Ze^2/r)\phi(x) , \tag{5.3}$$

where

$$r \equiv ba_0 x/Z^{1/3} , \tag{5.4a}$$

$$b \equiv (1/2)(3\pi/4)^{2/3} ; \tag{5.4b}$$

ϕ, x, and b are dimensionless. Since $V(r) \sim -Ze^2/r$ as $r \sim 0$, we have

$$\phi(0) = 1 . \tag{5.5}$$

Using Eqs. (5.3), (5.4), and (5.5) in Eq. (4.21), we arrive at the dimensionless form of the TF differential equation,

$$\frac{d^2\phi(x)}{dx^2} = \frac{\phi^{3/2}(x)}{x^{1/2}}, \quad \phi(x) > 0 , \tag{5.6a}$$

$$\frac{d^2\phi(x)}{dx^2} = 0, \quad \phi(x) \le 0 . \tag{5.6b}$$

One of the two boundary conditions necessary, in addition to Eq. (5.6), to uniquely define $\phi(x)$ is that given by Eq. (5.5). In arriving at Eq. (5.6) we used $\phi(x) = 1 + [\phi(x) - 1]$ to obtain

$$\nabla^2\left[\frac{\phi(x)}{r}\right] = \nabla^2\left[\frac{1}{r}\right] + \frac{1}{r}\frac{d^2\phi(x)}{dr^2} .$$

We can of course combine Eqs. (5.6a) and (5.6b) into the one equation

$$\frac{d^2\phi}{dx^2} = \frac{\{\max[\phi(x),0]\}^{3/2}}{x^{1/2}} . \tag{5.7}$$

We shall later need to know the behavior of $\phi(x)$ for very small x, and we therefore record the result

$$\phi(x) \sim 1 + x\phi'(0) + (4/3)x^{3/2} + O(x^2), \quad x \sim 0 , \tag{5.8a}$$

a consequence of Eqs. (5.5) and (5.6a); the value of $\phi'(0)$ is yet to be determined. It follows from Eq. (5.3) that

$$V(r) \sim -(Ze^2/r) + [\epsilon_F - Z^{4/3}\phi'(0)(e^2/ba_0)] + O(r^{1/2}) , \quad r \sim 0 . \tag{5.8b}$$

2. Neutral atoms

a. The value of the Fermi energy ϵ_F and the physical interpretation of that value

For positive ions, $V(r)$ behaves asymptotically as a Coulomb potential. It follows, as noted in Sec. I, that for positive ions we cannot have $p_F^2(r)/(2m_e) + V(r) = 0$, that is, $\epsilon_F = 0$, since $N = \int n(r)d\tilde{r}$, which is proportional to $\int p_F^3(r)d\mathbf{r}$, would be proportional to $\int[-V(r)]^{3/2}d\mathbf{r}$, and would therefore be infinite. The divergence would be at a more rapid rate if we had $\epsilon_F < 0$. Since ϵ_F cannot be positive if the electrons are not to escape to infinity, the only possibility that remains is that there is a value $r_0 < \infty$ beyond which $n(r) = 0$. We shall briefly pursue this further in a moment. [The positive-ion problem is discussed—if not always completely—in many texts. It cannot be scaled, as the neutral-atom problem can, and it cannot be handled analytically; further, the model of the atom in which the electron-electron interaction does not exist is a problem which also contains a region in which $n(r) = 0$ but which *can* be solved analytically, and which we shall have occasion to discuss in both this and the next section.]

The situation for the neutral atom is quite different. As opposed to the situation for a real neutral atom, the potential seen at large distances in a neutral atom in the TF approximation is not Coulombic. Now $\int[-V(r)]^{3/2}d\mathbf{r}$ is finite provided $V(r)$ falls off faster than r^{-2}. There is, then, no *a priori* reason for not having $\epsilon_F = 0$ for the neutral-atom case, nor is there any reason for not having $n(r) > 0$ for all r but $r = \infty$ for that case. To check for self-consistency, we note that we then have, using Eqs. (4.9e), (4.11), (4.16a), and (5.3), each with $\epsilon_F = 0$, (5.4) and (5.6a),

$$\begin{aligned} N &= (8\pi/3h^3)\int[-2m_e V(r)]^{3/2}d\mathbf{r} \\ &= (32\pi^2/3h^3)(2m_e Ze^2)^{3/2}(ba_0/Z^{1/3})^{3/2} \\ &\quad \times \int \phi^{3/2}(x)x^{1/2}dx \\ &= Z\int \phi''(x)x\,dx , \end{aligned}$$

with x ranging from 0 to ∞. Integrating by parts, using $\phi(0) = 1$, $\phi'(0) < \infty$, $\phi(x) \sim 0$, and $x\phi'(x) \sim 0$ as $x \sim \infty$, we do indeed find $N = Z$.

The statement that $n(r) > 0$ for $r \ne \infty$ implies $\epsilon_F = 0$, for Eq. (4.13a) is then valid for all finite r, and $\mu = -\epsilon_F = 0$ follows on letting $r \sim \infty$. The fact that ϵ_F and therefore μ has the value zero has an interesting physical interpretation, which was pointed out to me by E. Lieb. For $\mu = 0$, that is, for a vanishing Lagrange multiplier, the constraint $\int n(r)d\mathbf{r} = Z$ plays no role whatsoever. The solution for $n(r)$ obtained for $\mu=0$, which is the solution for a neutral atom, is the lowest-energy solution, for the fixed number of protons Z, for *any* value of $\int n(r)d\mathbf{r}$. On physical grounds, it is clear that the binding energy increases monotonically with N as N increases from 0 to Z. (Recall that we can take N to be a continuous variable. It might be preferable conceptually to take eN rather than N, that is, the total electronic charge rather than the total number of electrons, to be the continuous variable.) Further, we have argued that negative ions could not readily exist in the TF approximation, and the $\mu=0$ result "confirms" that argument. [Never having proved that there exists an $n(r)$ that minimizes the Lenz energy function, we have not proved anything, but the discussion will probably satisfy most physicists.]

Consider $n(r)$ versus r for fixed Z for three values of N: a value $N<Z$, the value $N=Z$, and a value $N>Z$. The solution for $N<Z$ vanishes for $r\geq r_0$, where $r_0=r_0(N)<\infty$, and a small change in $n(r)$ can give a first-order error. The solution for $N=Z$ does not fall off exponentially, as for a real atom, but falls off slowly, because the outermost electron does not experience a Coulomb attraction. It is simple to see that Eq. (5.6a) has as one solution (Sommerfeld, 1932), physically acceptable only for large x,

$$\phi(x)=144x^{-3} ,$$

where the normalization factor 144 is uniquely determined, the TF equation being nonlinear; the exact solution of $\phi(x)$, for $N=Z$, approaches this function for $x\sim\infty$. There is no physically acceptable solution for $N>Z$.

Having concluded that at most Z electrons can be bound to the nucleus, we find it reasonably clear, physically though not mathematically, that the TF equation for $n(\mathbf{r})$ does not have a unique solution if $N>Z$; the energy will, however, be seen to be unique. Thus, for $N>Z$, having placed Z electrons near the nucleus, we must decide where to place the remaining $N-Z$ electrons—or, equivalently in the TF context, the remaining (continuous) charge $(N-Z)e$—if the energy is to be minimized. We surely expect to have to place that charge at great distances from the nucleus. Since there is then no electron-nuclear interaction, the problem reduces to the minimization of the sum of the kinetic-energy term and of the e^-e^- term, both positive. The lowest energy of the residual charge will therefore be zero, so that in TF theory $E(N>Z)=E(N=Z)$, and is achieved by any distribution in which the residual charge density is everywhere arbitrarily small. Some further insight may be gained by considering models for which the minimum energy associated with the residual charge differs from zero. Thus, following Lieb (1981), we consider the Thomas-Fermi-Dirac (TFD) model, in which we account for the exchange potential energy, to be discussed in Sec. X.B, by adding a term

$$\tilde{E}_{\text{ex}}[n]=-C_{\text{ex}}\int n^{4/3}(r)d\mathbf{r}$$

to the Lenz energy functional of Eq. (4.9), where C_{ex} is a fixed positive constant. One again finds that at most Z electrons can be bound in the nucleus and that the residual charge $Q\equiv(N-Z)e$ should be far from the nucleus to minimize the energy of the residual charge. With n_Q the charge density associated with Q, we must now minimize not $\tilde{E}_K[n_Q]+\tilde{E}_{ee}[n_Q]$, as in the analysis of the energy of the residual charge in TF theory, but $\tilde{E}_K[n_Q]+\tilde{E}_{ee}[n_Q]+\tilde{E}_{\text{ex}}[n_Q]$, and since $\tilde{E}_{\text{ex}}$ is a negative term, the minimum energy of the residual charge need no longer be zero. Rather, the minimum is achieved by dividing Q into a very large number ν_q of widely separated very small charges $q=Q/\nu_q$. The contribution of the $\tilde{E}_{ee}[n_Q]$ term will then be found to be of lower order, it being bilinear in n_Q while the other terms are proportional to $n_Q^{5/3}$ and $n_Q^{4/3}$, respectively—having made this assumption, we can check it for self-consistency after the solution for $n_Q(r)$ has been obtained—and the problem reduces to the minimization of the energy of ν_q isolated charges,

$$\tilde{E}_Q[n_q]=\nu_q(\ )=(N-Z)\left\{(\ )/\int n_q(\mathbf{r})d\mathbf{r}\right\} ,$$

where

$$(\ )=\left\{(k\hbar^2/m_e)\int n_q^{5/3}(\mathbf{r})d\mathbf{r}-C_{\text{ex}}\int n_q^{4/3}(\mathbf{r})d\mathbf{r}\right\} ,$$

and where $n_q(\mathbf{r})$ is the number density of one of the charges. Since the integrands contain no explicit coordinate dependence but are functionals of n_q only, the minimizing equation will involve only n_q, and the solution for each small charge must be of the form $n_q=\text{const}\equiv\bar{n}>0$ in some volume τ and $n_q=0$ elsewhere. The integrations are now entirely trivial, $\{\ \}$ is a simple function of $\bar{n}$, and minimizing with respect to $\bar{n}$, one finds in the TFD model

$$E(N>Z)=E(N=Z)-C(N-Z) ,$$

with $C>0$ a known constant. This result is clearly completely unphysical—isolated electrons cannot have a total energy that is negative. Obviously one cannot use an approximation such as Thomas-Fermi-Dirac blindly, however useful it may be in some applications. A review of the above treatment shows the source of the error: ν_q is so large that the charge $Q=(N-Z)e$ is broken down into pieces with charge q smaller than that of an electron—indeed, so much smaller that the ν_q (positive) self-energy terms become negligible.

b. The ground-state energy E of a neutral atom

By the virial theorem—see the following subsection—we have $E=-E_K$. Using Eqs. (4.16a) and (5.3) with $\epsilon_F=0$, and Eq. (5.4a), we have

$$\begin{aligned} E &= -\int\int 2\frac{d\mathbf{r}\,d\mathbf{p}}{h^3}\frac{p^2}{2m_e} \\ &= -\frac{16\pi^2}{5m_e h^3}(2m_e Ze^2)^{5/2}\left[\frac{ba_0}{Z^{1/3}}\right]^{1/2} J \\ &= \frac{-16}{5\pi}(2b)^{1/2}Z^{7/3}\frac{e^2}{2a_0}J \ , \\ J &\equiv \int_0^\infty \phi^{5/2}(x)x^{-1/2}dx \ . \end{aligned}$$

If we evaluate J on the one hand by using Eq. (5.6a) and then integrating by parts, and on the other hand by integrating by parts, using Eq. (5.6a), and integrating by parts again, we find

$$\begin{aligned} J &= -\phi'(0) - \int_0^\infty [\phi'(x)]^2 dx \\ &= \tfrac{5}{2}\int_0^\infty [\phi'(x)]^2 dx \ . \end{aligned}$$

It follows from this last equation that we can write

$$J = -(5/7)\phi'(0) \ .$$

Using Eq. (5.4b), we find that

$$E = (16/7\pi)(3\pi/4)^{1/3}\phi'(0)Z^{7/3}(e^2/2a_0) \ . \tag{5.9a}$$

Writing

$$e^2/2a_0 = \mathrm{Ry} \ , \tag{5.9b}$$

the Rydberg, and inserting the value of $\phi'(0)$ for the neutral atom determined numerically by Tal and Levy (1981) by demanding that the solution of Eq. (5.7) vanish at ∞, we obtain the result

$$E = -c_7 Z^{7/3}\mathrm{Ry}, \quad c_7 = 1.537\,490\,24\ldots \ . \tag{5.9c}$$

[The notation c_7 as the coefficient of the $Z^{7/3}$ term in E is useful in expressing the leading terms in E in an expansion of powers of $Z^{-1/3}$ as $(-c_7 Z^{7/3} - c_6 Z^{6/3} - c_5 Z^{5/3})\mathrm{Ry}$.]

c. Relations among the three contributions to E

It is often simply assumed that the virial theorem, valid of course for a real atom, is valid in the TF approximation, but it is not obvious that this is the case. The proof is simple (Lieb, 1981). With $n(r)$ representing the number density that minimizes E, we introduce a scaling factor s and define a scaled number density,

$$n_s(r) = s^3 n(sr) \ . \tag{5.10}$$

By construction $n_s(r)$ has the same normalization as $n(r)$, and we find immediately from the definitions given in Eqs. (4.9b)–(4.9d) that

$$\begin{aligned} \tilde{E}[n_s] &\equiv \tilde{E}_K[n_s] + \tilde{E}_{ev}[n_s] + \tilde{E}_{ee}[n_s] \\ &= s^2\tilde{E}_K[n] + s(\tilde{E}_{ev}[n] + \tilde{E}_{ee}[n]) \\ &= s^2 E_K + s[E_{ev} + E_{ee}] \ . \end{aligned}$$

The value of s that minimizes $\tilde{E}[n_s]$ follows from differentiation of this last expression and is given by

$$2sE_K + (E_{ev} + E_{ee}) = 0 \ .$$

But since n is the number density that minimizes E, the value of s that minimizes $\tilde{E}[n_s]$ is $s=1$, and we therefore have

$$2E_K + (E_{ev} + E_{ee}) = 0 \ , \tag{5.11}$$

which is just the usual virial theorem.

We can find a second relation among the components of E. For the neutral atom under consideration, Eq. (4.13a), with $\mu=0$, is valid for all r. Multiplying by $n(r)$, integrating over $d\mathbf{r}$, and comparing with Eqs. (4.9b)–(4.9d), we obtain

$$\tfrac{5}{3}E_K + E_{ev} + 2E_{ee} = 0 \ . \tag{5.12}$$

Comparing Eqs. (5.11) and (5.12), we find a result first obtained by Fermi:

$$E_K : -E_{ev} : E_{ee} = 3:7:1 \ . \tag{5.13}$$

As opposed to the virial theorem result given in Eq. (5.11), which is exact for all Z, Eq. (5.12) and therefore Eq. (5.13) become exact only when the TF approximation becomes exact, that is, only for $Z \sim \infty$.

The virial theorem result of Eq. (5.11) is independent of the TF approximation, and it is natural to ask if the result $E_{ev}/E_{ee} = -7$ can be obtained *without* invoking the TF apparatus. We need two relations between E_K, E_{ee}, and E_{ev}, and we saw in Sec. III that we can find two relations among energy components if the problem has two lengths to be determined, but the atom has only one such length, its radius R. (In a more detailed analysis, there are a number of other lengths, such as the skin depth of the surface, but the contributions to the energy of the regions defined by these lengths are of lower order than the $Z^{7/3}$ term under consideration.) There does, however, exist an elegantly simple procedure, pointed out by A.R.P. Rau (unpublished) and Thirring (1983), for obtaining the ratio -7. Essential features of TF theory are that the lowest energy, for fixed nuclear charge Ze, is that with $N=Z$ electrons, and that $\epsilon_F=0$, and it turns out that those are the *only* TF features required to get the desired ratio. In other words, we can completely ignore TF theory and simply assume those features on the basis of our knowledge of real atoms and ions. (There are of course negative ions in nature, and ϵ_F is not identically zero, but we need merely assume that the number of electrons *beyond* Z which can be bound is of lower order than Z, and that ϵ_F is negligible.) Our starting point is now not a functional, but simply the function $\tilde{E}(R)$ given by Eq. (4.3). The equation was derived for the case of Z electrons, and we modify it to allow an arbitrary number N of electrons. In addition, we insert the coefficients c', $\tilde{c}$, and $\bar{c}$, which are assumed to be independent of N and Z and are expected to be positive and of order unity; the values of these coefficients need not be known in advance in the present rederivation of the result given in Eq. (5.13). For fixed Z, we then have

$$\tilde{E}(R,N)=c'N^{5/3}(\hbar^2/m_eR^2)-(\tilde{c}NZ-\bar{c}N^2)e^2/R \; . \tag{5.14}$$

The ratio of E_{ev} to E_{ee} is then $(-\tilde{c}Z/\bar{c}N)$, which is $-\tilde{c}/\bar{c}$ for $N=Z$. Since the effective potential must be attractive for $N\leq Z$, we must find $\tilde{c}/\bar{c}>1$; in fact, we now show that the assumptions that there are no negative ions and that $\epsilon_F=0$ lead to the desired result, that $-\tilde{c}/\bar{c}=-7$. To minimize the expression for $\tilde{E}(R,N)$, we first set

$$\partial\tilde{E}(R,N)/\partial R=0$$

and find that

$$R=2c'[N^{2/3}/(\tilde{c}Z-\bar{c}N)]a_0 \; .$$

(This reduces to the correct functional form $a_0/Z^{1/3}$ for $N=Z$.) Inserting this value of R into $\tilde{E}(R,N)$ gives

$$E(N)=-[\bar{c}^{\,2}/2c']N^{1/3}[(\tilde{c}/\bar{c})Z-N]^2\mathrm{Ry} \; .$$

In line with our assumption about negative ions we set $dE(N)/dN=0$ at $N=Z$, and this immediately gives

$$\tilde{c}=7\bar{c} \; , \tag{5.15a}$$

as desired.

It is amusing to go a bit further. For $N=Z$ and $\tilde{c}=7\bar{c}$, $E(N)$ reduces to

$$E=-[18\bar{c}^{\,2}/c']Z^{7/3}\mathrm{Ry} \; .$$

We have not yet used the TF approximation in any way. We now use that approximation by setting

$$18\bar{c}^{\,2}/c'=c_7 \; , \tag{5.15b}$$

in order to obtain the TF estimate of the energy of the system; E then becomes exact for $Z\sim\infty$. Equations (5.14) and (5.15) give

$$\tilde{E}(R,N)=\frac{18\bar{c}^{\,2}}{c_7}\frac{N^{5/3}\hbar^2}{m_eR^2}-\bar{c}(7NZ-N^2)\frac{e^2}{R} \; . \tag{5.16a}$$

This relatively simple expression for $\tilde{E}(R,N)$ is based on (i) a form of the kinetic energy that follows from the uncertainty principle and the exclusion principle, (ii) a knowledge of the energy of a neutral atom for $Z\sim\infty$, and (iii) the knowledge that negative ions barely exist, if at all. $\tilde{E}(R,N)$ has some nice features:

(α) As can be seen by inspection, it gives $E_{ev}=-7E_{ee}$ for $N=Z$.

(β) Since it is of the form $(a/R^2)-(b/R)$, it satisfies the usual virial theorem, giving $2E_K+E_{ev}+E_{ee}=0$. Combined with the result given in (α), it therefore reproduces the $3{:}-7{:}1$ ratio of Eq. (5.13).

(γ) Minimization with respect to R gives

$$R=g(N/Z)a_0/Z^{1/3} \; , \tag{5.16b}$$

where

$$g(y)=(36\bar{c}/c_7)y^{2/3}/(7-y) \; . \tag{5.16c}$$

(For $N=Z$, this gives R proportional to $a_0/Z^{1/3}$, the TF result, but with an unspecified coefficient.) For R given by Eq. (5.16b), $\tilde{E}(R,N)$ reduces to

$$E(N)=f(N/Z)E_{\mathrm{TF}} \; , \tag{5.16d}$$

where

$$E_{\mathrm{TF}}=-c_7Z^{7/3}\mathrm{Ry}$$

and

$$f(y)=y^{1/3}(7-y)^2/36 \; .$$

Note that $E(N=Z)=E_{\mathrm{TF}}$.

$E(N)$ is also of the form of Eq. (5.16d) in TF theory, as shown for example in March (1975), but in TF theory $f(N/Z)$ must be calculated numerically.

(δ) There are no negative ions. Note that the above results did not require the specification of $\bar{c}$, but while the energy E associated with $\tilde{E}(R,N)$ of Eq. (5.16a) is independent of $\bar{c}$, for E obtained by minimization with respect to R—that has to be so, since we can scale out $\bar{c}$ by simply defining a new length, equal to $R/\bar{c}$—other properties are not independent of $\bar{c}$; $\bar{c}$ can be fixed by demanding agreement with some other atomic property, but we shall not do so.

The "classical" Hamiltonian $\tilde{E}(R,N)$, of Eq. (5.16a) becomes a quantum-mechanical (hydrogenlike) Hamiltonian $H(R,N)$ if we reverse the usual procedure and replace $\hbar^2/R^2$ by $\mathbf{p}^2=-\hbar^2\nabla^2$. We then have

$$H(R,N)=-\frac{18\bar{c}^{\,2}}{c_7}\frac{N^{5/3}\hbar^2\nabla^2}{m_e}-\bar{c}(7NZ-N^2)\frac{e^2}{R} \; . \tag{5.16e}$$

$H(R,N)$ also gives the results (α) through (δ) noted just above.

It should be stressed that while the relationship $2E_K+E_V=0$ is entirely independent of the choice of the c', $\tilde{c}$, and $\bar{c}$, the same is *not* true of the relationship $E_{ev}+7E_{ee}=0$, the derivation above notwithstanding, for we have assumed that the coefficients are such that the energy minimum as a function of N, for Z fixed, is at $N=Z$.

We have now given two arguments that the ratio of $-E_{ev}$ to E_{ee} is 7, one based on TF theory and one starting from Eq. (5.14). The result is a very important one since it provides considerable insight into why an effective central potential works so well. We shall therefore try briefly to provide some further physical understanding of the factor 7. We have

$$\begin{aligned}-E_{ev}/E_{ee}&=Z\times\tfrac{1}{2}Z^2\langle e^2/r\rangle/\langle Ze^2/r_{12}\rangle\\&=\tfrac{1}{2}\langle 1/r\rangle/\langle 1/\mathbf{r}_{12}\rangle \; .\end{aligned}$$

For a uniform spherical distribution, we readily find that $-E_{ev}/E_{ee}=2.5$, far from the factor 7. In actuality, of course, the electron distribution is far from uniform, being heavily concentrated toward the origin. As a very simple model of a nonuniform distribution, assume that a fraction f of the electrons is close to the nucleus and has a uniform spherical distribution, and that the remainder are relatively far from the nucleus. We then have $-E_{ev}/E_{ee}=2.5/f$, larger than 2.5.

3. Properties of $n(r)$ for positive ions

Thomas-Fermi theory is much less appealing for ions than for neutral atoms, the element of universality having been largely lost, but, as it happens, there are more ions than neutral atoms, so let us proceed.

Equations (4.14), (4.16a), and (5.3) lead immediately, for the spherically symmetric case of interest, to

$$n^{2/3}(r)=\frac{3}{5k}\frac{Z}{a_0 r}\phi(x), \quad \text{where } n(r)>0 \ . \qquad (5.17)$$

We define

$$N(r)=\int_0^r n(r')4\pi(r')^2 dr' \qquad (5.18)$$

and note that $N(0)=0$ since $\phi(0)=1$, so that $n(r')$ is proportional to $(r')^{-3/2}$ for $r'\sim 0$. [That $n(0)$ is infinite is, of course, an unfortunate property of TF theory.] $N(r)$, the number of electrons within a sphere of radius r centered on the nucleus, is a monotonically increasing function where $n(r)>0$, and $N(\infty)=N$. We rewrite Eq. (4.20) as

$$\nabla^2\left[\frac{5k\hbar^2}{3m_e}n^{2/3}(r)-\frac{Ze^2}{r}\right]=4\pi e^2 n(r) \ ,$$

$$\text{where } n(r)>0 \ . \qquad (4.20')$$

Using Eqs. (5.17) and (5.8a), we find that the quantity within the large parentheses in Eq. (4.20′) is well behaved at the origin. Integrating Eq. (4.20′) over a sphere of radius r centered at the origin, we find, with R_0 the ionic radius—$n(r)>0$ if and only if $r<R_0$—

$$\frac{5k}{3}a_0 r^2\frac{dn^{2/3}(r)}{dr}=N(r)-Z, \quad r\le R_0 \ , \qquad (5.19)$$

or

$$\frac{dn(r)}{dr}=\frac{9}{10k}\frac{N(r)-Z}{r^2 a_0}n^{1/3}(r), \quad r\le R_0 \ . \qquad (5.20)$$

Equation (5.20) shows immediately (once again) that we cannot have a negative ion in the TF approximation, for by assumption we would then have $N(\infty)=N>Z$, so that there would necessarily be an $R<\infty$ such that $N(R)=Z$; we would therefore have $dn/dr>0$ for $r>R$, and finally we would *not* have $n(\infty)=0$. For positive ions, we have seen that there exists a value R_0, where $0<R_0<\infty$, such that $n(r)=0$ for $r\ge R_0$ [and $n(r)>0$ for $r<R_0$]. We must have $N(r)=N$ for $r\ge R_0$ [and $N(r)<N$ for $r<R_0$]. Since $n(R_0)=0$, we see from Eq. (5.20) that

$$\left.\frac{dn}{dr}\right|^{r=R_0}=0 \ .$$

Using $dN(r)/dr=4\pi r^2 n(r)$, we find on differentiating Eq. (5.20) that

$$\frac{d^2n}{dr^2}=-\frac{2}{r}\frac{dn}{dr}+\frac{1}{3n}\left[\frac{dn}{dr}\right]^2+\frac{18\pi}{5k}\frac{n^{4/3}}{a_0} \ .$$

At $r=R_0$, the first and third terms vanish, and, using Eq. (5.20), we are left with

$$\left.\frac{d^2n}{dr^2}\right|^{r=R_0}=\frac{27}{100k^2a_0^2R_0^4}\left.\frac{[N(r)-Z]^2}{n^{1/3}(r)}\right|^{r=R_0} ,$$

where r is to approach R_0 from below. Since $N(R_0)=N<Z$ and $n(R_0)=0$, the second derivative is infinite, which is hardly surprising, since $n(r)$ vanishes for $r\ge r_0$ but does not vanish for $r<R_0$.

On the basis of previous discussions, we do not expect to have R_0 finite for $N=Z$, that is, we then expect to have $n(r)$ vanish only at infinity and to vanish smoothly. Without proving anything, we simply observe that for $N=Z$, even allowing for the possibility that R_0 is finite, we have $N(R_0)-Z=0$; to obtain d^2n/dr^2 at $r=R_0$ we must therefore evaluate $\{N(r)-Z\}^2/n^{1/3}(r)$ at $r=R_0$ by means of de l'Hôpital's rule. Doing so, we find that d^2n/dr^2 is proportional to $n^{4/3}(r)$ at $r=R_0$ and therefore is not infinite but rather vanishes. Indeed, *all* derivatives of $n(r)$ and indeed $n(r)$ itself vanish at $r=R_0$ for $N=Z$.

C. Independent-particle model for atoms and ions

We turn our attention now from real atoms and ions to an independent-particle model for atoms and ions in which the electron-electron interaction does not exist. (This solvable model will be useful when one considers the leading corrections to TF theory.) The functional $\tilde{E}[n]$ for this model follows from the $\tilde{E}[n]$ of Eq. (4.9) on simply omitting the double integral $\tilde{E}_{ee}[n]$ term. The differential equation for $n(r)$ obtained by seeking the minimum of the modified version of $\tilde{E}[n]$ is then that given by Eq. (4.20) with the $-4\pi e^2 n(r)$ term omitted. The analog of Eq. (5.19) is obtained by simply omitting the $N(r)$ term; we therefore have

$$\frac{dn^{2/3}(r)}{dr}=-\frac{3Z}{5ka_0r^2}, \quad r\le R_0 \ . \qquad (5.21)$$

Integrating, we arrive at

$$n^{2/3}(r)=(3Z/5ka_0)[(1/r)+\text{constant}], \quad r\le R_0 \ .$$

To satisfy $n(R_0)=0$, we set the constant equal to $-(1/R_0)$. We then have

$$n(r)=\{(3Z/5ka_0)(1/r-1/R_0)\}^{3/2}, \quad r\le R_0 \ . \qquad (5.22)$$

The value of R_0 follows from the normalization condition of Eq. (4.9e) and is given by

$$R_0=(2a_0/Z)(3N/2)^{2/3} \ . \tag{5.23}$$

We record the result—a consequence of the vanishing of $n(r)$ and therefore of $p_F(r)$ at $r=R_0$—

$$\frac{p_F^2(r)}{2m_e}-\frac{Ze^2}{r}=-\frac{Ze^2}{R_0} \ . \tag{5.24}$$

The explicit solution for $n(r)$ given by Eqs. (5.22) and (5.23) has the following properties:

(α) As opposed to the case for real atoms, there is a TF bound solution for *all* N, that is, for $N<Z$, for $N=Z$, *and* for $N>Z$. (Since there is no e^-e^- interaction, it is clear that the nucleus can bind an infinite number of electrons, each in a hydrogenic state.) We also have $R_0<\infty$ for all N.

(β) $n(R_0)$ vanishes by construction, for all N. Taking derivatives, we also have $dn/dr=0$ at $r=R_0$ for all N, while $d^2n/dr^2=\infty$ at $r=R_0$ for all N.

We have studied the model as a special case of the atom. It would have been simpler to study the model directly, since we know immediately that $V(r)=-Ze^2/r$ for all r, for any N.

To obtain the ground-state energy E of our model, in the TF approximation, we can proceed along the same lines as for a real atom, and we can therefore omit most of the steps. Beginning with the virial theorem, and using Eq. (5.24), we have

$$\begin{aligned} E&=-\int\int\frac{2d\mathbf{r}\,d\mathbf{p}}{h^3}\frac{p^2}{2m_e} \\ &=-\frac{2}{5\pi m_e\hbar^3}(2m_eZe^2)^{5/2}J' \ , \end{aligned}$$

where

$$\begin{aligned} J'&\equiv\int_0^{R_0}\left[\frac{1}{r}-\frac{1}{R_0}\right]^{5/2}r^2dr \\ &=\frac{5\pi}{16}R_0^{1/2} \ , \end{aligned}$$

with R_0 given by Eq. (5.23). We therefore have as the TF approximation for our model ion

$$E_{\rm TF}(\text{model ion})=-2Z^2(3N/2)^{1/3}\text{Ry} \ . \tag{5.25a}$$

For $N=Z$, we therefore have

$$E_{\rm TF}(\text{model atom})=-2(3/2)^{1/3}Z^{7/3}\text{Ry} \ . \tag{5.25b}$$

The Z dependence is the same as for the real atom in the TF approximation. The TF energy estimate of Eq. (5.25a)—and the special case in Eq. (5.25b)—give the leading term of the true ground-state energy exactly. Thus, for $N\gg1$, there will be a maximum principal quantum number $Q\gg1$ associated with the last closed shell, defined by

$$N=\sum_1^Q 2n^2\approx\tfrac{2}{3}Q^3 \ , \tag{5.26}$$

where $2n^2$ is the degeneracy factor and where, for simplicity only, we ignore the relatively few electrons that may be present in an open shell with principal quantum number $Q+1$. To lowest order the true ground-state energy is then

$$\begin{aligned} \sum_1^Q(2n^2)(-)\frac{Z^2e^2}{2a_0n^2}&=-\frac{Z^2e^2}{a_0}Q \\ &=-\frac{Z^2e^2}{a_0}\left[\frac{3N}{2}\right]^{1/3} \ , \end{aligned} \tag{5.27}$$

in agreement with Eq. (5.25a). The TF estimate of R_0 given in Eq. (5.23) also agrees, to leading order, with the exact result, but an additional element of care is required. The expectation value of r in the hydrogenic state with quantum numbers n and l is

$$\langle r\rangle_{nl}=[3n^2-l(l+1)]a_0/(2Z)\le 3n^2a_0/(2Z) \ .$$

The weighted average $\langle r\rangle_n$ of $\langle r\rangle_{nl}$ with respect to l is therefore $\langle r\rangle_n<3n^2a_0/(2Z)$, and, in particular, we have, to leading order,

$$\langle r\rangle_Q<3Q^2a_0/2Z=(3a_0/2Z)(3N/2)^{2/3}=(3/4)R_0 \ .$$

It is scarcely surprising that $\langle r\rangle_Q$ is less than R_0, since $\langle r\rangle_Q$ is a weighted average with respect to l of the mean value of r for principal quantum number Q, while R_0 is the distance beyond which (in the TF approximation) $n(r)$ vanishes identically. For $Q\gg1$, the bulk of the electrons will have large orbital angular momenta, and it will be adequate to approximate the exact hydrogenic densities by their WKB approximations. As is to be expected and as was shown by, for example, Shakeshaft and Spruch (1979), one readily finds that the WKB approximation approaches the classical density, that associated with ellipses. For a given value of Q, the energy is independent of l, or, speaking classically, the energy is determined by the semimajor axis, being independent of the semiminor axis. For $l\approx n=Q$, $\langle r\rangle_{Ql}$ is approximately a circle of radius Q^2a_0/Z. For $1\ll l\ll Q$, the energy remains the same and therefore the semimajor axis remains the same, Q^2a_0/Z, while the semiminor axis becomes negligible, and the elliptic orbit approaches a straight line of length $2Q^2a_0/Z$, with the nucleus at the end point. Thus, to leading order, the furthest away an electron can be found will be

$$2Q^2a_0/Z=(2a_0/Z)(3N/2)^{2/3}=R_0 \ ,$$

the desired result. Finally, we note that to lowest order the estimate of the Fermi energy

$$\epsilon_F=-\frac{Ze^2}{R_0}=-\frac{Z^2e^2}{2a_0(3N/2)^{2/3}}=-\frac{Z^2e^2}{2a_0Q^2} \ ,$$

which follows from Eqs. (5.24), (5.23), and (5.26), is, as it should be, the energy of an electron in the outermost shell.

D. Thomas-Fermi theory in a D-dimensional space

Thomas-Fermi theory in D-dimensional space can arise from a study of a particular problem in three-dimensional space in the TF approximation, which, in a further approximation, leads to a TF-like approximation in D dimensions. Thus, for low-Z atoms or ions in the strong B field of a pulsar, the Coulomb field plays a significant role only with respect to motion of the electrons parallel to $\mathbf{B}$, and one obtains a $D=1$ TF-like result. We shall elaborate on this in Sec. VII. Alternatively, one can study TF theory in D dimensions in the hope of shedding light on the $D=3$ TF theory. In this case there is some freedom in the approach to be used. The two most natural possibilities are to continue to interpret the Coulomb potential as $1/r$, with r now defined by $r^2=\sum_i (x_i^2)$ with $1 \le i \le D$ and with $1/|\mathbf{r}-\mathbf{r}'|$ analogously defined, *or* to interpret $1/r$ as the Green's function defined by

$$\nabla^2 G(\mathbf{r}) = -4\pi\delta^{(D)}(\mathbf{r})$$

and the usual boundary conditions, with $\mathbf{r}$ D-dimensional and $\delta^{(D)}(\mathbf{r})$ the D-dimensional delta function. Similarly, $1/|\mathbf{r}-\mathbf{r}'|$ is to be interpreted as $G(\mathbf{r}-\mathbf{r}')$. We then have (Gelfand and Shilov, 1964)

$$G(r)=\begin{cases} -2\pi r, & D=1 \\ -2\ln r, & D=2 \\ 4\pi r^{2-D}/[(D-2)\Omega_D], & D \ge 3 \ , \end{cases}$$

where

$$\Omega_D = D\pi^{D/2}/\Gamma(\tfrac{1}{2}D+1)$$

is the solid angle in D dimensions, that is, the area of the D-dimensional unit hypersphere. We use $g(\mathbf{r})=g(r)$ to represent $1/r$ or $G(r)$ and $g(\mathbf{r}-\mathbf{r}')$ to represent $1/|\mathbf{r}-\mathbf{r}'|$ or $G(\mathbf{r}-\mathbf{r}')$.

In extending $\tilde{E}[n]$ of Eq. (4.9) to the D-dimensional case, we replace the three-dimensional r in (the spherically symmetric) $n(r)$ by the D-dimensional r, the three-dimensional d^3r by the D-dimensional volume element $d^Dr, 1/r$ by $g(r)$, and $1/|\mathbf{r}-\mathbf{r}'|$ by $g(\mathbf{r}-\mathbf{r}')$. Further, with $p_F=p_F(r)$ the upper limit on p, we now have

$$n(r)=2\int d^Dp/h^D = 2(\Omega_D/D)(p_F/h)^D \ ,$$

while Eq. (4.9b) is replaced by

$$\tilde{E}_K[n]=\int \frac{2d^Dr\,d^Dp}{h^D}\frac{p^2}{2m_e} = k_D\frac{\hbar^2}{m_e}\int [n(r)]^{(D+2)/D} d^Dr \ ,$$

where

$$k_D = 2\pi^2[D/(D+2)](D/2\Omega_D)^{2/D} \ .$$

Consider the choice $g=G$. This case was analyzed by Kventsel and Katriel (1981), who obtained analytic solutions for both neutral atoms and positive ions for $D=2$ (the spectra for $D=2$ are discrete) and found, for $D \ge 4$, that $n(r)$ is not integrable at the origin. We shall examine only the $D \ge 4$ result. The authors used the differential TF equation approach, but we shall use the Lenz-energy-functional approach because it more clearly exhibits the physical aspects of the problem. Since we have a spherically symmetric situation, we can replace the $1/|\mathbf{r}-\mathbf{r}'|^{D-2}$ factor in $G(\mathbf{r}-\mathbf{r}')$ by

$$\langle 1/|\mathbf{r}-\mathbf{r}'|^{D-2}\rangle \equiv \int (1/|\mathbf{r}-\mathbf{r}'|^{D-2}) d^D\Omega/\Omega_D \ .$$

Since $|\mathbf{r}-\mathbf{r}'|=[r^2+(r')^2-2rr'\cos\theta]^{1/2}$ is independent of the $D-2$ angle variables ϕ_j, which, with the length and polar angle, define $\mathbf{r}$, the ϕ_j dependent factors cancel. Using material in Sommerfeld (1949) one can then show, with $r_>$ the larger of r and r', that

$$\left\langle \frac{1}{|\mathbf{r}-\mathbf{r}'|^{D-2}} \right\rangle = \frac{1}{(r_>)^{D-2}} \le \frac{1}{r^{D-2}} \ .$$

As for $D=3$, the inequality is intuitively reasonable on geometrical grounds. It follows that, as for $D=3$, $\tilde{E}_{ee}[n] < \tilde{E}_{ev}[n]$. To prove that there is no acceptable solution for the Lenz energy functional for a given D, it will suffice therefore to show that there exists an $n(r)$ which, for that D, leads to finite values of $E_K[n]$ and N but to $-\infty$ for E_{ev}. It is trivial to show that the choice $n(r) \sim 1/r^q$ for $r \sim 0$, with $2 \le q < D^2/(D+2)$—q then exists for $D \ge 4$ but *not* for $D=3$—and $n(r) \sim 0$ sufficiently rapidly as $r \sim \infty$ for the various integrals to converge at infinity, leads to the values stated.

The analysis seems not to have been carried out for the choice $g(r)=1/r$, but it is simple to show that $\tilde{E}[n]$ is not bounded from below for $D=1$. This follows from the choice $n(r) \sim 1/r^q$ as $r \sim 0$ for $D-1 \le q < D^2/(D+2)$; q then exists for $D=1$.

[Parenthetically, we note that the anthropic principle might suggest that space must be three dimensional (Hawking, 1988). Thus a space with $D=2$ might not allow systems as complicated as people to develop—Hawking gives an amusing argument—while for $D>3$ the orbits of systems bound by a $1/r$ potential, whether gravitationally bound planets or Coulombically bound electrons, are unstable.]

E. An application: photoabsorption by cesium

The very strong emphasis of the present paper on general results and insights might unfortunately give the impression that there have been few down-to-earth applications of TF theory. In fact, there have been myriads of such applications. We shall discuss an application that utilizes a model potential, since many of the applications utilize such potentials. Our one example should give some flavor of the nature of those applications. That example concerns photoabsorption by cesium; we shall give only a brief sketch of a calculation by Norcross (1973), who used a two-parameter semiempirical model potential based on the lowest few spectroscopic term values.

The potential in the wave equation for the radial part of the wave function of the outer electron is taken to be

$$V(\lambda,r)+V_p(r)+V_{\rm so}(r) \; .$$

The scaled TF potential $V(\lambda,r)$ generated by the core in the absence of the outer electron is supplemented by $V_{\rm so}(r)$, a spin-orbit potential, and by $V_p(r)$, a polarization potential. $V_p(r)$ represents the effect of the moments in the core induced by the outer electron and is taken to be

$$V_p(r)=\frac{\alpha_d}{r^4}[1-f^6(r)]+\frac{\alpha_q-6\beta a_0}{r^6}[1-f^{10}(r)] \; .$$

Here $f(r)\equiv\exp(-r/r_c)$, α_d and α_q are the static electric dipole and quadrupole polarizabilities of the core, and β is a nonadiabatic electric dipole core polarizability, a measure of the inability of the induced core dipole moment to respond instantaneously to the motion of the outer electron. The cutoff radius $r_c=r_c^{(l)}$, a function of the orbital angular momentum l of the outer electron, is, for a given l, one of the open parameters; it is of the order of the radius of the core. The leading terms in $V_p(r)$ for r well beyond r_c, where the outer electron is primarily situated, behave as r^{-4} and r^{-6}; the coefficients α_d and $\alpha_q'\equiv\alpha_q-6\beta a_0$ of these terms are formally exact, and there is available a fair amount of information concerning α_d and α_q'. The forms of the cutoff factors have been chosen to give $V_p(r)$ the appropriate dependence on r for r small. $V_{\rm so}(r)$ is given by

$$V_{\rm so}(r)=\tfrac{1}{2}\alpha^2\frac{1}{r}\frac{dV}{dr}[1+\tfrac{1}{4}\alpha^2V(r)]^{-2}\mathbf{L}\cdot\mathbf{S} \; ,$$

where α is the fine-structure constant, $V(r)\equiv V(\lambda,r)+V_p(r)$, and the square bracket term is an additional relativistic correction which gives $V_{\rm so}(r)$ the proper behavior near the origin. The details of how to choose the form of $V(\lambda,r)$ can be found in Eissner and Nussbaumer (1969), who chose a modified TF potential based on a description given by Gombás (1956).

With λ, $r_c^{(0)}$, and $r_c^{(1)}$ approximately chosen, Norcross obtained excellent agreement with the experimentally determined energies of the low-lying states $ns_{1/2}$, $np_{1/2}$, and $np_{3/2}$, for $n=6$, 7, 8, and 9. With the effects of V_p accounted for in both the model potential and the dipole transition matrix element, and *without* normalizing to any experimental data on photoabsorption, Norcross obtained very good agreement with the photoabsorption data. [Later work by Zhou and Norcross (1989), based on the Dirac rather than the Schrödinger equation, determines other properties of cesium but is not relevant to our discussion.]

In summary, the use of spectroscopic data to fit open parameters in a model potential seen by the outer electron, where the model potential utilized TF theory and incorporated as much of the physics as was known and deemed relevant, led to good agreement with photoabsorption data.

VI. NEUTRON STARS, WHITE DWARFS, AND THE DIVERGENCE OF PERTURBATION SERIES IN QUANTUM ELECTRODYNAMICS

The discussion in Sec. V can be adapted readily to simple models of neutron stars and white dwarfs, assuming the thermal energy and nuclear interactions to be negligible and the nonrelativistic approximation to be valid. The subject of divergences in quantum electrodynamics might seem to lie outside of the domain of TF theory. Nevertheless, an understanding of the presumed origin of the divergence requires an estimation, which can be quite crude, of the energy of systems of particles of imaginary charge, an estimation quite similar to that for neutron stars. In any event, the argument, which is due to Dyson (1952), is so simple and beautiful that the reader not familiar with it might be pleased by the digression. We shall consider neutron stars and white dwarfs first. The numbers of papers on these subjects, if not quite comparable to the number of such stars, is large. For the moment we arbitrarily cite only Orear and Salpeter (1973) on neutron stars, and Van Horn (1979) on white dwarfs, for introductory treatments, and Thirring (1983) and Shapiro and Teukolsky (1983) for advanced and comprehensive treatments of both. There are two not unrelated points to consider at the outset.

(α) There are two kinds of charged particles in both the white dwarf and the atom, namely, nuclei and electrons, and the kinetic energy in each case is almost entirely that of the light particle. The reasons are not quite the same. Roughly speaking, in the atom the nucleus is subject to a set of pairwise interactions, $-Ze^2/r_{ij}$, no larger than and indeed equal to the largest of the pairwise interactions to which the ith electron is subject, namely, the same electron-nucleus interaction; the momenta of the nucleus and of an electron can therefore be expected to be comparable, and the kinetic energies of the nucleus and of an electron can be expected to be inversely proportional to their masses. In the white dwarf, on the other hand, the nuclei are subject to gravitational interactions, the largest of which are larger than the largest of the gravitational interactions to which electrons are subject by a factor equal to the ratio of their masses, and one has to be more careful if one is to justify the neglect of the nuclear kinetic energies. In the white dwarf the Coulomb interaction of a pair of (point) particles is, of course, many many orders of magnitude greater than the gravitational interaction of a pair, with the repulsive Coulomb interactions tending to dominate over the attractive Coulomb interactions. (If the positive and negative charges were each continuous and if the net charge were zero, an approximation we shall later make in our zeroth-order estimate of the energy, the minimum energy would be identically zero and would be achieved for perfect charge neutrality.) This places a high premium on having near-perfect charge neutrality at the local level, and there is indeed near-perfect local charge neutrality for a large enough number of particles. (To lowest order there is, therefore, no Coulomb interaction.) This in turn demands that the spatial distribution be almost the same for the two sets of particles. The nuclei and the electrons therefore have the same uncertainty in position and therefore the same uncertainty in momentum, and, thus, the same characteristic momentum. Their kinetic energies therefore vary inversely with their masses. One finds the curious but readily understandable result—see (β) immediately below—that despite the fact that the Coulomb pair interaction so dominates the gravitational pair interaction, the energy of the white dwarf does not to lowest order depend upon the charge of the electron nor of the nucleus. This does *not* imply that the Coulomb interaction plays no role; as we shall see, the energy of the white dwarf would be very different if there were no Coulomb interaction.

(β) The totally dominant interaction in the atom, pairwise or overall, is the Coulomb interaction, that between electrons and that between electrons and the nucleus. In the neutron star and in the white dwarf the dominant overall interaction is the gravitational interaction between nuclei; the smallness of the gravitational relative to the Coulomb interaction *pairwise* is more than compensated for, for a sufficiently large number of particles, by the fact that the Coulomb interactions are both attractive and repulsive and therefore saturate, while all gravitational interactions are of one sign.

A. Neutron stars: the ground-state energy

We begin with a neutron star, assumed for simplicity to consist exclusively of neutrons, N_n in number. With $n(r)$ now the neutron number density, and m_n the neutron mass, $\tilde{E}[n]$ is obtained from Eq. (4.9a) by replacing m_e by m_n, dropping the $\tilde{E}_{e\nu}[n]$ term, and replacing e^2 in the $\tilde{E}_{ee}[n]$ term by $-Gm_n^2$, with G the gravitational constant; in Eq. (4.9e) we replace N by N_n. Though the terminology is never used, we then have a TF theory of a neutron star, a theory that has been shown by Hertel, Harnhofer, and Thirring (1972) to be exact in the limit $N_n \sim \infty$, assuming the nonrelativistic theory to be valid in that limit. Corresponding changes can be made in the more rudimentary form, Eq. (4.3). Replacing m_e by m_n, $Z^{5/3}$ by $N_n^{5/3}$, and Z^2e^2 by $N_n^2Gm_n^2$, one immediately finds by minimization [or by the appropriate replacements in Eq. (4.4)] that

$$R(\text{neutron star}) \approx \frac{\hbar^2}{m_n(Gm_n^2)} \times \frac{1}{N_n^{1/3}} \equiv \frac{a_n}{N_n^{1/3}} , \tag{6.1a}$$

$$E(\text{neutron star}) \approx -\frac{G^2m_n^5N_n^{7/3}}{\hbar^2} = -N_n^{7/3}\frac{Gm_n^2}{a_n} . \tag{6.1b}$$

Formula (6.1a) can be rewritten in an interesting form involving the mass M(neutron star)$=m_nN_n$ of the neutron star, where we ignore the correction to the mass associated with the binding energy of the neutron star, a reasonable procedure since we are assuming the nonrelativistic approximation to be moderately accurate. We find

$$M(\text{neutron star})R^3(\text{neutron star}) \approx \hbar^6/(G^3m_n^8) , \tag{6.1c}$$

the right-hand side containing only fundamental constants.

A quite different approach is possible for neutron stars. This approach is unrelated to the TF approximation but, since the argument is short and since it is so pretty, it would be almost immoral not to mention it. We have

$$H = \sum_{i=1}^{N_n} p_i^2/2m_n - \sum_{1\le i<j\le N} Gm_n^2/r_{ij} . \tag{6.2}$$

As a further refinement of a trick of Fisher and Ruelle (1966), reformulated by Dyson and Lenard (1967, 1968), Lévy-Leblond (1969) rewrites Eq. (6.2) as

$$H = \sum_{i=1}^{N_n} \left[\sum_{j\neq i} [p_j^2/2(N_n-1)m_n - Gm_n^2/2r_{ij}] \right]$$

$$\equiv \sum_{i=1}^{N_n} h_i . \tag{6.2$'$}$$

Here h_i represents the Hamiltonian of N_n-1 particles $(j\neq i)$ of inertial mass $(N_n-1)m_n$ and gravitational mass $m_n/2$ in the gravitational field of one fixed particle, the ith, with gravitational mass m_n; the N_n-1 particles do not interact with one another. The ground state of h_i is the state in which the neutrons occupy the N_n-1 lowest hydrogenlike energy levels. The (degenerate) energy levels of h_i are given, letting $e^2 \to G(\frac{1}{2}m_n)m_n$ and $m_e \to (N_n-1)m_n$ in the usual hydrogenic expressions, by

$$\epsilon_q = -(N_n-1)(G^2m_n^5/\hbar^2)/(8q^2), \quad q=1,2,\ldots ;$$

the corresponding hydrogenlike radii are

$$r_q = q^2\hbar^2/[(N_n-1)m_n(Gm_n^2/2)] .$$

By using the lowest eigenvalues for each h_i and summing, we do *not* obtain the lowest eigenvalue of H, for we then, incorrectly, treat the h_i as independent, whereas the h_i have common coordinates. We *do*, however, obtain a rigorous lower bound $\underline{E}$(neutron star) on the ground-state energy of H. [As an interesting variant of the above type of inequality, consider two distinguishable particles interacting with one another and with a center of force; in an obvious notation we have

$$H = T_1 + V_1(r_1) + [T_2 + V_2(r_2) + V_{12}(r_{12})] .$$

We can obtain a lower bound on the ground-state energy E_{gd} of the system by solving (numerically) a sequence of two one-body problems; one involves two centers. Thus we freeze particle number 1 at a distance r_1 from the center of force and determine the ground-state energy $\mathcal{E}_{\text{gd}}(r_1)$ of particle 2 in the potential generated by particle 1 and the center of force. Since

$$T_2+V_2(r_2)+V_{12}(r_{12})\geq \mathscr{E}_{\rm gd}(r_1)\ , \tag{6.3}$$

the ground-state energy of $T_1+V_1(r_1)+\mathscr{E}_{\rm gd}(r_1)$ provides a lower bound on $E_{\rm gd}$. This simple theorem, with minor variants, has been used to prove that certain systems, such as e^++H (Aronson *et al.*, 1971) and e^++He (Gertler *et al.*, 1968), cannot form a bound state. It can also be used (Hahn and Spruch, 1974) to obtain a lower bound on some scattering lengths. The theorem provides one of the few means available by which one can attempt to prove the nonexistence of bound states.] Lévy-Leblond preserves the rigorous lower bound on the ground-state energy E(neutron star) by using further inequalities, but to avoid a bit of algebra we shall be satisfied with an estimate of $\underline{E}$(neutron star). Since there is a degeneracy factor $2q^2$ associated with the energy level ϵ_q, we write

$$N_n=\sum_{i=1}^{Q}2q^2\approx 2Q^3/3\ , \tag{6.4}$$

where we have assumed that N_n is so large that Q, the highest principal quantum number associated with a fully occupied state, satisfies $Q\gg 1$, and we have ignored the relatively few neutrons in the state with principal quantum number $Q+1$. We then have

$$\begin{aligned}E(\text{neutron star})\geq \underline{E}(\text{neutron star})&\approx N_n\sum_{q=1}^{Q}2q^2\epsilon_q\\ &\approx -(N_n^2/4)(G^2m_n^5/\hbar^2)Q\\ &\approx -(1/4)(3/2)^{1/3}N_n^{7/3}(G^2m_n^5/\hbar^2)\ ;\end{aligned}$$

the N_n in front of the sum accounts for the number $(N_n-1)(\approx N_n)$ of h_i's. We also have

$$R(\text{neutron star})\approx r_Q\approx 2(3/2)^{2/3}N_n^{-1/3}(\hbar^2/Gm_n^3)\ .$$

These results are of course of the same form as those of Eq. (6.1).

The estimate of $\underline{E}$—better, the rigorous lower bound $\underline{E}$ on E—has recently been improved by a method that entails no additional effort (Basdevant, Martin, and Richard, 1989). Thus, rather than starting with the identity

$$\sum_{i=1}^{N_n}p_i^2=\sum_{i=1}^{N_n}\sum_{j\neq i}p_j^2/(N_n-1)$$

used in obtaining Eq. (6.2′), one starts with the identity

$$\sum_{i=1}^{N_n}p_i^2=\frac{1}{N_n}\left[\sum\sum_{i<j}(\mathbf{p}_i-\mathbf{p}_j)^2+\left[\sum_i \mathbf{p}_i\right]^2\right]\ .$$

The term $\sum_i \mathbf{p}_i$ is the momentum of the center of mass and can be dropped; it is the elimination of the energy of the motion of the center of mass of the pair which represents the advantage of the new form of $\sum_i p_i^2$. The canonical momentum conjugate to $\mathbf{r}_i-\mathbf{r}_j$ is not $\mathbf{p}_i-\mathbf{p}_j$ but $\frac{1}{2}(\mathbf{p}_i-\mathbf{p}_j)\equiv\boldsymbol{\pi}_{ij}$. We can now write

$$H=\sum\sum_{i<j}\left[\frac{4(\boldsymbol{\pi}_{ij})^2}{2mN_n}-\frac{Gm_n^2}{r_{ij}}\right]\ . \tag{6.2″}$$

This approach can be very useful for small values of N_n. If we are interested in large values of N_n and ignore the difference between N_n and N_n-1, Eq. (6.2″) generates a lower bound on the energy which represents an improvement by a factor of 2 over that obtained from Eq. (6.2′).

The brief remarks above concern only the most rudimentary aspects of neutron stars. There are presently under way investigations of the origin of neutron stars—we shall have one brief comment on this later—of the changing structure of a neutron star from the origin to the surface and to the plasma region beyond, of the effect of the intense magnetic field, of the accretion of mass onto a neutron star when it is one component of a binary, etc. (One can almost expect that in the near future there will be universities with Departments of the Interiors of Neutron Stars, and Departments of the Exteriors of Neutron Stars.)

There has recently been considerable interest in the possible existence of stars consisting of bosons. The determination to within a numerical constant of order unity of an upper limit on the mass of a boson star, for bosons of mass m_B interacting gravitationally, follows easily. Proceeding along the lines used often above, we consider the ultrarelativistic approximation and, since the Pauli principle does not apply, approximate the total kinetic energy of N_B bosons in a sphere of radius R by $N_Bpc\approx N_B\hbar c/R$. The total energy is then $[N_B\hbar c-G(N_Bm_B)^2]/R$, and we have collapse when the square bracket vanishes. The maximum mass of a boson star is then

$$M_{\rm max}(\text{boson star})\approx \hbar c/Gm_B\ .$$

Proceeding more formally, we assume the Hamiltonian to be the semirelativistic form $H_R(m_B,N_B,\gamma_j=Gm_B^2)$ used by Martin (1988a, 1988b; see Sec. III.B.2) in obtaining the collapse condition of an atom. One can bound H_R by the sum of a known term and a nonrelativistic Hamiltonian H_{NR} as Martin did, and eliminate the kinetic energy of the center of mass of each pair, as discussed just above. Using an upper bound on the ground-state energy of H_{NR}, obtained by a Rayleigh-Ritz calculation, Basdevant, Martin, and Richard (1989) find as an upper limit on the mass of a boson star

$$M(\text{boson star})<1.51(\hbar c/Gm_B)\ .$$

The numerical coefficient is not much more than twice the value, 0.633, obtained in previous general-relativistic calculations of the bound. (The term "mini-boson star" is often used, since, for the values of m_B expected to be relevant, $M_{\rm max}$ is so much smaller than the mass of a typical star.)

B. White dwarfs: the ground-state energy

In studying a white dwarf, we assume for simplicity that it consists of N electrons, with number density $n(r)$, and the same number N of protons with mass m_p. Further, in line with remarks (α) and (β) above, we assume that the protons have the same number density $n(r)$; this will be justified somewhat more formally later. Presumably, we have thereby almost fully accounted for Coulomb interactions, which we henceforth ignore in the preliminary treatment of white dwarfs in this subsection. $\tilde{E}[n]$ for the white dwarf is then obtained from Eq. (4.9a) by replacing m_e by m_p in the $\tilde{E}_K[n]$ term, dropping the $\tilde{E}_{ev}[n]$ term, and replacing e^2 in the $\tilde{E}_{ee}[n]$ term by $-Gm_p^2$; in Eq. (4.9e) we replace Z by N. For a simpler rougher estimate, we could in Eq. (4.3) replace $Z^{5/3}$ by $N^{5/3}$, and Z^2e^2 by $N^2Gm_p^2$; m_e remains as is. (Recall that the kinetic energy is that of the electrons, while the potential energy is that of the protons.) Minimizing the simpler version of $\tilde{E}(R)$ thereby obtained, we find

$$R(\text{white dwarf}) \approx \hbar^2/(Gm_e m_p^2 N^{1/3}) \equiv a_p/N^{1/3} , \qquad (6.5a)$$

$$E(\text{white dwarf}) \approx -N^{7/3}G^2 m_e m_p^4/\hbar^2 = -N^{7/3}\frac{Gm_p^2}{a_p} . \qquad (6.5b)$$

The "Bohr radii," a_p of Eq. (6.5a) and a_n of Eq. (6.1a), are quite different, their ratio being (on setting $m_n = m_p$)

$$a_n/a_p = m_e/m_p . \qquad (6.5c)$$

With M(white dwarf)$\approx m_p N$, the mass of the white dwarf, Eq. (6.5a) can be rewritten as

$$M(\text{white dwarf})R^3(\text{white dwarf}) \approx \hbar^6/(G^3 m_e^3 m_p^5) . \qquad (6.5d)$$

As for neutron stars, we neglect mass corrections associated with the binding energy.

In arriving at Eqs. (6.5) we assumed that there are so many protons that the (nonsaturating) gravitational interactions of the protons dominate over all Coulomb interactions of protons and electrons, but we have as yet made no estimate of the critical number of protons that must be present if that is to be the case. As will be seen in the next subsection, it will be true for neutral systems with the number of nuclei of the order of or larger than the number of nuclei in planets. (Their odd, nonspherical shapes make it clear that gravitational interactions have not yet taken over for objects the size of asteroids.) Indeed, Coulomb interactions might seem at first blush to play no role whatever for white dwarfs, since the charge e does not enter Eqs. (6.5), but in fact Coulomb interactions play a decisive role, as suggested by the presence of m_e in Eqs. (6.5). If protons and electrons were uncharged, the uncharged protons and uncharged electrons would remain coupled, but only by their gravitational interaction, and a white dwarf composed of uncharged protons and electrons would consist of a small uncharged proton star embedded in a much larger uncharged electron star; there would be two spherical distributions, with the same center. The properties of the uncharged proton star would be almost independent of the presence of the uncharged electron star. R(unch.proton star) and E(unch.proton star) would be obtained from Eqs. (6.1) by simply replacing N_n by N and m_n by m_p. (If the protons were uncharged, m_n and m_p would presumably be equal; for equal numbers of neutrons and protons, our uncharged proton star would, ignoring the negligible gravitational effect of the uncharged electrons, be identical to a neutron star.) From Eqs. (6.1a), (6.1b), and (6.5a)–(6.5c) it follows that, for a comparable number of nucleons, R(unch.proton star) would be very much smaller than R(white dwarf), by the factor m_e/m_p, while E(unch.proton star) would be very much larger than E(white dwarf), by the factor m_p/m_e. While the uncharged electrons would scarcely affect the uncharged protons, the converse would not be true; the gravitational field generated by the small uncharged proton star would be the dominant attractive force forming the uncharged electron star.

We can reword the above discussion as follows. In a white dwarf composed of N protons and N electrons, with N sufficiently large, the Coulomb force so dominates at the local level that the white dwarf can be thought of as consisting of N neutral (spin-1/2) fermions, each with the inertial mass of the lighter particle, m_e, and each with the gravitational mass of the heavier particle, m_p. The argument can be readily extended. To quote Lévy-Leblond (1969), "even when the nuclei obey Bose statistics, the exclusion principle operating on the electrons to limit their density is 'transmitted' to the nuclei by the interplay of Coulomb forces." It is therefore entirely trivial to generalize the above treatment of an electron-proton model of a white dwarf to a white dwarf model in which the protons are replaced by alpha particles, or by an arbitrary but specified mixture of protons, alpha particles, . . . ; the electrons generate the kinetic energy and the nuclei the gravitational potential energy. For the particular case of $N = N_Z Z$ electrons and N_Z nuclei of charge Ze and mass m_Z, Eq. (4.3) is replaced by

$$\tilde{E}(R) \approx (N_Z Z)^{5/3}(\hbar^2/m_e R^2) - N_Z^2 G m_Z^2/R ,$$

while Eqs. (4.4), or Eqs. (6.5), are replaced by

$$R(\text{white dwarf}) \approx Z^{5/3}\hbar^2/(Gm_e m_Z^2 N_Z^{1/3}) , \qquad (6.5a')$$

$$E(\text{white dwarf}) \approx -N_Z^{7/3}G^2 m_e m_Z^4/(Z^{5/3}\hbar^2) . \qquad (6.5b')$$

As noted in the Introduction, the TF model is not applicable to our Sun, since there the kinetic energy originates not in the exclusion principle but in thermal motion.

C. White dwarfs: the critical numbers

We turn now to the estimation of the critical number of nuclei, N_{crit}(nuclei) and N'_{crit}(nuclei), which must be present if the gravitational interactions are to begin to dominate over the Coulomb interactions at the *interatomic* and *intra-atomic* levels, respectively. In the former case only the outer electrons are in states quite different from the outer electron states in normal matter, while in the latter case even the inner electrons are in states quite different from the inner electron states in normal matter. In both cases, the gravitational force rather than the Coulomb force has become the origin of the cohesiveness of matter. We first consider the interatomic case. We make the rough assumption, which should be sufficiently accurate for our purposes, that the binding energy of a pair of "compressed atoms"—the energy measured with respect to the sum of the energies of two isolated "compressed atoms"—is of the order of the binding energy of the last electron of an isolated "compressed atom"; this in turn is of the order of the Coulomb energy of the last electron. N_{crit}(nuclei) is then the number of nuclei for which the total gravitational potential energy of the system begins to dominate over the sum of the Coulomb energies of the last electrons for all of the "compressed atoms." We begin by considering the case for which all of the nuclei are protons. Since each "compressed hydrogen atom" has only one electron, one cannot speak of inner and outer electrons, but our treatment of the proton case is the analog, for heavy nuclei with many electrons, of the *interatomic* case. (For heavy nuclei, we shall study the interatomic case by considering just one electron for each "compressed atom," the outermost electron, and we shall study the intra-atomic case by considering the Z electrons in each "compressed atom" statistically.) If the N protons and N electrons are in a sphere of radius R, the gravitational energy will be of the order of

$$\tilde{E}_{\text{grav}}(R) \approx -N^2 G m_p^2 / R \ . \tag{6.6}$$

The average nearest-neighbor distance r_0 will then be defined roughly by $N r_0^3 \approx R^3$. Taking into account the self-screening property of electrostatic interactions, as noted by Dyson and Lenard (1967)—see the discussion of Onsager's theorem in Sec. VIII.B—we see that the Coulomb energy will be of order

$$\tilde{E}_{\text{Coul}}(R) \approx -N(e^2/r_0) \approx -N^{4/3}(e^2/R) \ . \tag{6.7}$$

Equating the two energies gives

$$N_{\text{crit}}(\text{protons}) \approx (e^2/G m_p^2)^{3/2} \approx 10^{54} \ . \tag{6.8}$$

N_{crit}(protons) is the number of protons (and of electrons) at which the *interatomic* bonds begin to be overcome by the gravitational forces.

An almost identical analysis is applicable to the interatomic case for matter consisting of N_Z nuclei of charge Ze, mass number A, and mass m_Z, and of $N_Z Z$ electrons. We assume that we can describe matter as consisting of atoms with almost all of the electrons in an atom in an inert core, and with a number of order unity of electrons in an atom that are not rigidly bound to the nucleus. The Coulomb energy of the inner electrons is irrelevant to an analysis of interatomic bonds; the relevant Coulomb energy will therefore remain of the order of that given in Eq. (6.7). The above analysis is then valid if we merely replace m_p by m_Z, so that we have

$$N_{\text{crit}}(\text{nuclei}) \approx (e^2/G m_Z^2)^{3/2} \ . \tag{6.9}$$

We turn now to an estimation of the value of the second critical number, N'_{crit}(nuclei), for which the *intra-atomic* bonds begin to be overcome by gravitational forces, the inner as well as the outer electrons no longer being in bound states attached to the nucleus. Assuming again that we have N_Z atoms of nuclear charge Ze and mass m_Z, we can obtain the gravitational energy from Eq. (6.6) by simply replacing m_p by m_Z and N by N_Z, so that we now have

$$\tilde{E}_{\text{grav}}(R) \approx -N_Z^2 G m_Z^2 / R \ . \tag{6.10}$$

The intra-atom Coulomb energy is a sum of the individual atomic energies. Each "atom" is now confined to a cell, which we take to be a sphere of radius R_{cell} with the nucleus at the center, where R_{cell} varies from point to point, as it is determined by the local number density. A characteristic value of R_{cell} is given by $R_{\text{cell}} = N_Z^{-1/3} R$, and will be significantly smaller than a_0. The Coulomb energy of an "atom" will not therefore be of order $-Z^{7/3} e^2 / R_{\text{cell}}$, as might be expected for a normal atom. Rather, the Coulomb energy of the "atom" will be of order $-Z^2 e^2 / R_{\text{cell}}$, for at the very high electron densities in a white dwarf the Coulomb field is not very effective and the electron density will be nearly uniform over the dimension of an "atom." We shall give some more details on this point in Section VI.E. (The distinction between the Coulomb energy of an atom and an "atom" has sometimes been missed in the literature. Of course, there is not that much difference normally between $Z^{7/3}$ and Z^2, and the argument is in any event a crude one.) We have

$$\tilde{E}_{\text{Coul,intra}}(R) \approx -N_Z Z^2 (e^2 / R_{\text{cell}}) \approx -Z^2 N_Z^{4/3} (e^2/R) \ . \tag{6.11}$$

Equating Eqs. (6.10) and (6.11) gives

$$N'_{\text{crit}}(\text{nuclei}) \approx Z^3 N_{\text{crit}}(\text{nuclei}) \ . \tag{6.12}$$

For ironlike matter with $Z \approx 25$ and $m_Z \approx 10^{-22}$ g, not too bad a description of the matter of the inner planets, we find $N_{\text{crit}}(\text{nuclei}) \approx 10^{49}$, with an associated mass $\approx 10^{27}$ g. This is indeed of the order of the masses of the inner planets, for which we know that both the gravitational and Coulombic interactions are important. As noted earlier, Coulombic interactions dominate for objects of the order of asteroids; on the other hand, gravitational interactions dominate for objects of the order of white dwarfs.

Lévy-Leblond (1969) not only presented much of the above heuristic proof but gave a rigorous proof, starting with a Hamiltonian that contains nuclear and electronic kinetic energies and Coulombic and gravitational interactions.

We close this subsection with some brief historical remarks on white dwarfs. To begin, we note that *in the very year of the introduction of the Schrödinger equation,* Fowler (1926) realized that "a star was like a giant molecule in its ground state," with the zero-point pressure of the electrons preventing collapse of the star. The realization that gravitational pressure could overcome the zero-point pressure in the relativistic domain—for much the same reason that a one-electron ion collapses for Z large enough in relativistic theory but not in nonrelativistic theory—was first recognized by Frenkel (1928) and, with some errors, by Anderson (1920); neutron star collapse is discussed in the next subsection. Further advances include work by Stoner (1930), Chandrasekhar (1931a, 1931b), and Landau (1932). In a lecture at the Erice Summer School, Thirring, in a brief account of the early history of stability which includes the above comments, also observes that "none of the authors so far mentioned quotes any of the previous work on that problem." *Plus ça change, plus c'est la même chose.* The great theoretical activity had little experimental data to serve as guidance; though many young astrophysicists think of white dwarfs as having been known to Hipparchus, they were first observed in the 1910s, and as of 1940 there were of the order of half a dozen white dwarfs that had been reasonably carefully observed. As late as the 1950s, few if any physics texts gave the white dwarf as the magnificent example that it is of the dramatic effects of the Pauli exclusion principle. Theory and experiment and text books have since made great strides. In theory, one is concerned with many matters such as the formation, structure, and evolution of white dwarfs, and with the effect of the strong magnetic field on the polarization of the radiation emitted. Those interested in the history of science might look at pages 506 through 509 of Kobold (1926), which indicates some of the ideas about white dwarfs that were prevalent *before* the currently accepted concepts were introduced; the ideas should but probably will not give pause to some sure-of-themselves present-day theorists.

D. On the collapse of neutron stars and white dwarfs

We noted in Sec. III.B.2 that the method used there to obtain a bound on the collapse condition for an atom (or a collection of atoms) could also be used to study the collapse of a neutron star or a white dwarf. We shall here approach the question rather differently; to obtain a very rough estimate of the conditions for the collapse of a neutron star or of the white dwarf, we proceed in the ultrarelativistic approximation, along the lines we used in studying the collapse of a one-electron ion. For the neutron star, with each neutron in a small sphere of radius r_0, with $p \approx \hbar/r_0$, and all N_n neutrons in a large sphere of radius $R=N_n^{1/3}r_0$, we have

$$\begin{aligned}\tilde{E}(R) &\approx N_n pc-(N_n^2 G m_n^2/R)\\ &\approx (N_n^{4/3}\hbar c-N_n^2 G m_n^2)/R\ .\end{aligned}$$

We therefore have collapse if

$$N_n \gtrsim (\hbar c/G m_n^2)^{3/2} \equiv N'\ .$$

The neutron star mass beyond which the gravitational attraction overwhelms the repulsion originating in the exclusion principle is therefore—ignoring binding-energy corrections, no longer such a reasonable approximation—

$$\begin{aligned}M(\text{collapse neutron star}) &\approx N' m_n = (\hbar c/G)^{3/2} m_n^{-2}\\ &\approx 10^{33}\,\text{g} \approx M_\odot\ ,\end{aligned} \tag{6.13}$$

where $M_\odot$ is the mass of our sun. For the white dwarf, with N_Z nuclei of atomic energy Z and mass m_Z defining the gravitational energy, and $N=ZN_Z$ electrons defining the (ultrarelativistic) kinetic energy, we have $R=N^{1/3}r_0$, with r_0^3 the volume associated with an electron, and

$$\begin{aligned}\tilde{E}(R) &\approx Npc-N_Z^2(G m_Z^2/R)\\ &\approx [Z^{4/3}N_Z^{4/3}\hbar c-N_Z^2 G m_Z^2]/R\ .\end{aligned}$$

We therefore have collapse if

$$N_Z \gtrsim Z^2(\hbar c/G m_z^2)^{3/2} \equiv N''\ .$$

The mass beyond which a white dwarf will collapse, the Chandrasekhar mass M_{Ch}, is therefore given—ignoring binding-energy corrections—by

$$M_{\mathrm{Ch}} \approx m_Z N'' = (\hbar c/G)^{3/2}(Z/m_Z)^2\ .$$

If our nucleus of atomic number Z has a mass number $A \approx 2Z$, we have $m_Z \approx A m_n \approx 2Z m_n$, and therefore, dropping a factor 1/4,

$$M_{\mathrm{Ch}} \approx (\hbar c/G)^{3/2} m_n^{-2} \approx M_\odot\ . \tag{6.14}$$

We make a few small remarks.

(α) In general we have

$$n(r)=(8\pi/3h^3)p_F^3(r) \approx [p_F(r)/\pi\hbar]^3\ .$$

For the ultrarelativistic approximation to be reasonably accurate we require $p_F \gg m_e c$ for the white dwarf and $p_F \gg m_n c$ for the neutron star. We therefore require

$$n(r) \gg (m_e c/\pi\hbar)^3 \quad \text{for the white dwarf ,}$$

$$n(r) \gg (m_n c/\pi\hbar)^3 \quad \text{for the neutron star .}$$

The condition on $n(r)$ for the neutron star is therefore much stronger than for the white dwarf, and indeed neutron stars are much smaller—compare Eqs. (6.1a) and (6.5a), valid for precollapse conditions. The masses at collapse are roughly the same.

(β) Our model of a white dwarf is somewhat more realistic than our model of a neutron star. The neutron star is far from consisting of neutrons alone, nuclear forces cannot be ignored, and even the effects of general relativity are not completely negligible.

(γ) If a white dwarf accretes mass slowly, it will build up to the Chandrasekhar mass M_{Ch} and then collapse, perhaps to a neutron star, and perhaps without much loss of mass. One might then expect to find neutron stars, at least those neutron stars which developed as just described, with masses very close to M_{Ch}. There is one binary that almost certainly consists of two neutron stars, each of which does have a mass very close to M_{Ch}.

(δ) Corrections to the TF approximation to the ground-state energy of an atom, which is of order $Z^{7/3}$Ry, are of order Z^2Ry. Since $Z^{-1/3}$ is hardly negligible for the Z's of interest, the TF approximation, while useful for the atomic insights it provides, may not provide an accurate estimate. In stars, on the other hand, one will be concerned with collections of particles of order $N=10^{57}$ or so, and the neglect of a correction of order 10^{-19} will be very tolerable.

(ϵ) For the white dwarf and neutron star, a particle at a great distance r from the center will experience an attractive $1/r$ potential, which is also the case for a positive ion. As for the positive ion, therefore, a white dwarf and a neutron star in the TF approximation will have $n(r)=0$ for r beyond some given point.

(ζ) For the neutral atom, with $N=Z$ electrons, one can scale the TF differential equation so that one solution is applicable to all Z. This is not the case for positive ions, for which one is concerned with Z *and* N. For neutron stars there *is* only one large number, the number N_n of neutrons, and for white dwarfs, which are assumed to be neutral, or essentially neutral, there is effectively only one number, N_Z, with the number of electrons then equal to ZN_Z. (The argument is almost identical for a specified mixture of nuclei.) One can therefore expect to be able to scale the TF-like equations for neutron stars and white dwarfs.

(η) As noted above, the Coulomb interaction in the white dwarf plays a fundamental role in keeping the electrons close to the nuclei. In addition, the Coulomb interaction makes a direct contribution to the energy, a small but not negligible correction which we shall now consider.

E. The Coulomb contribution to the energy of a white dwarf

1. The first Coulomb correction

Having solved numerically in a TF-like approximation the problem in which N electrons of inertial mass m_e generate the kinetic energy and $N_Z=N/Z$ nuclei of gravitational mass m_Z generate the gravitational potential energy, one knows the electron number density $n(r)$ and the nuclear number density $n(r)/Z$. Let the average electron number density in the neighborhood of some point r_P be $\bar{n}\equiv n(r_P)$. In that neighborhood, we know the effective volume τ occupied by each nucleus and its associated electrons. We surround each nucleus by a Wigner-Seitz cell, which we take to be simply a sphere of that radius R_{cell} which gives the volume τ. Up to this point, the nuclear and electronic charges have been assumed to be smeared out, neutralizing one another so that there are no electric fields. To account for Coulomb effects, we must be more realistic and take the nuclei and electrons to be point charges. Since the charge and mass distributions within each cell remain spherically symmetric, the interaction of any two cells is unaffected by the collapse within each cell of the nuclear charge to a point and of the electron charge to a set of Z points. The Coulombic and gravitational self-energies of point nuclei and point electrons define the zero-energy reference level and can therefore be omitted. The gravitational interaction between the nucleus and the electrons in any one cell and the change in that interaction under the collapse to points are negligible, and the determination of the charge correction reduces to the estimation of the Coulomb energy of a point nucleus at the center of a cell of specified radius R_{cell} and of a spherical distribution of neutralizing (point) electrons within that cell, with the charge distribution of the electrons to be that which minimizes the energy. Thomas-Fermi theory was used to estimate the energy in the zeroth-order approximation in which the charges were spread out, and TF theory can also be used to estimate the Coulomb correction. (Note, though, that in zeroth order all of the enormous number of electrons and nuclei are considered at once, and the TF estimate is effectively exact, while in the Coulomb correction one considers the cells one at a time and the TF estimate may not be very accurate, since the number of electrons in one cell, Z, is quite small.) Thus we could now set up a Lenz energy functional for a neutral atom confined to a sphere of radius R_{cell} by using Eqs. (4.9), with $N=Z$, restricting the range of integration from 0 to R_{cell}, and imposing the boundary condition $dn/dr=0$ at $r=R_{\text{cell}}$. (This last condition is a symmetry condition, which can most easily be understood by thinking of the case for which the cells are rectangular parallelopipeds.) The $n(r)$ that minimizes this Lenz functional would not scale, but would have to be solved numerically for different values of Z and $\bar{n}$ or, equivalently, of Z and R_{cell}. One can, however, obtain a simple reasonably accurate estimate of the Coulomb energy of the cell, for in the high-density limit the kinetic energy dominates and it is a good approximation to use $n(r)=\bar{n}$. The contribution associated with $E_K[\bar{n},R_{\text{cell}}]$ of Eq. (4.9b) is the kinetic energy that has already been considered; the corrections are $E_{ev}[\bar{n},R_{\text{cell}}]$ of Eq. (4.9c) and $E_{ee}[\bar{n},R_{\text{cell}}]$ of Eq. (4.9d). [We use E rather than $\tilde{E}$, since $n(r)$ and therefore $\bar{n}$ are known, so that the energies are not functions but numerical values.] These corrections are readily evaluated, for they are the usual expressions for the Coulomb energy of a uniformly charged sphere of total charge $-Ze$ interacting with a point charge Ze at the center and with itself, namely,

$$E_{ev}[\bar{n},R_{\text{cell}}]=-(3/2)Z^2e^2/R_{\text{cell}}\ , \tag{6.15a}$$

$$E_{ee}[\bar{n},R_{\text{cell}}]=(3/5)Z^2e^2/R_{\text{cell}}\ . \tag{6.15b}$$

For later reference, we record the ratio

$$-E_{ev}[\bar{n},R_{\text{cell}}]/E_{ee}[\bar{n},R_{\text{cell}}]=5/2\ . \tag{6.16}$$

The Coulomb correction per cell in the uniform density approximation, that is, the first-order correction $E^{(1)}$(cell), is the sum of the expressions in Eq. (6.15). We have

$$\begin{aligned}E^{(1)}(\text{cell})&=-(9/10)Z^2e^2/R_{\text{cell}}\\&=-(9/10)(4\pi\bar{n}/3)^{1/3}Z^{5/3}e^2\ ;\end{aligned} \tag{6.17}$$

in the second step we used

$$\bar{n}=Z/(4\pi R_{\text{cell}}^3/3)\ . \tag{6.18}$$

(Although the virial theorem is satisfied in the zeroth-order expression for the energy—the nuclear gravitational potential energy having twice the magnitude of the kinetic energy of the electrons—and although our first-order correction is a potential-energy term, the virial theorem is *not* violated. Sec Sec. III.C.1.) Dividing $E^{(1)}$(cell) by the volume $Z/\bar{n}$ of the cell gives the energy-density correction to first order, and, finally, replacing $\bar{n}$ by $n(r)$ and integrating over the volume of the white dwarf gives as the total first-order energy correction

$$E^{(1)}=-(4\pi/3)^{1/3}(9/10)Z^{2/3}e^2\int n^{4/3}(r)d\mathbf{r}\ . \tag{6.19}$$

The kinetic energy per cell was calculated as a zeroth-order term and will therefore be denoted by $E_K^{(0)}$(cell). Since $\bar{n}$ is a constant, it follows immediately from Eq. (4.9b) that

$$\begin{aligned}E_K^{(0)}(\text{cell})&\approx(\hbar^2/m_e)\bar{n}_{\text{cell}}^{5/3}R_{\text{cell}}^3\\&\approx e^2a_0Z^{5/3}/R_{\text{cell}}^2\ ,\end{aligned}$$

using Eq. (6.18) in the second step. Comparing this with $E^{(1)}$(cell) as given by the first form of Eq. (6.17), we have

$$E^{(1)}(\text{cell})/E_K^{(0)}(\text{cell})\approx Z^{1/3}(R_{\text{cell}}/a_0)\equiv p\ . \tag{6.20}$$

If our perturbation-theoretic approach is to be correct, this expansion parameter p must be small. Since a characteristic density in a white dwarf is 10^6g/cm^3, while a characteristic density of ordinary matter is of order unity, the volume per atom compared to the volume of an isolated atom will be reduced by a factor, very roughly, of 10^6, so that R_{cell}/a_0 will be of order 10^{-2} and p will indeed be small. $E^{(1)}$(cell) represents the second term in a power series in p for the TF energy of an atom confined by great pressure to a volume very much smaller than a_0^3. We shall calculate the third term in the expansion in the next subsection.

The ratio $E^{(1)}(\text{cell})/E_K^{(0)}(\text{cell})$ is equal to the ratio $E^{(1)}/E_K^{(0)}$ of their volume integrals. But, by the virial theorem, the total kinetic energy is equal in magnitude to the total energy E(white dwarf). It follows that

$$\begin{aligned}\frac{E^{(1)}}{E(\text{white dwarf})}&\approx\frac{Z^{1/3}R_{\text{cell}}}{a_0}\\&\approx\frac{Z^{1/3}R(\text{white dwarf})}{a_0N_Z^{1/3}}\\&\approx\frac{Z^2e^2}{Gm_Z^2N_Z^{2/3}}\ ,\end{aligned}$$

using Eq. (6.5a′) in the last step. The condition that this ratio is to be small compared to unity is nothing other than the condition $(N'_{\text{crit}}(\text{nuclei})/N_Z)^{1/2}\ll 1$, with the critical number defined by Eqs. (6.12) and (6.9); clearly, the perturbation must be small whether viewed at the cellular level or at the level of the entire white dwarf.

2. The second Coulomb correction

We can go beyond the leading Coulomb correction, that associated with the uniform density approximation, and determine, to next order, the Coulomb correction associated with the variation of the number density *within* the cell. With $\bar{n}$ the average number density within the cell—$\bar{n}$ will depend upon where in the white dwarf the cell is located—we write, with r here representing the distance from the center of the cell, where the nucleus is located,

$$n(r)=[1+q(r)]\bar{n}\ . \tag{6.21}$$

Here $q(r)$, to be determined, is assumed to be a perturbation. Since we have

$$\int n(r)d\mathbf{r}=\int\bar{n}\,d\mathbf{r}(=Z)\ ,$$

we must have

$$\bar{n}\int q(r)d\mathbf{r}=0\ .$$

We introduce

$$F[n]\equiv\tilde{E}_{\text{cell}}[n]+\mu\bar{n}\int q(r)d\mathbf{r}\ ,$$

where $\tilde{E}_{\text{cell}}[n]$ is defined by Eq. (4.9), but with the range of all integrals defined by the radius R_{cell} of the cell. We expand in $q(r)$, retaining terms of order $q^2(r)$ in the expansion of the dominant kinetic-energy term but only terms of order $q(r)$ in the potential-energy terms. We arrive at

$$\begin{aligned}F[n]&=E_{\text{cell}}[\bar{n}]+\tilde{E}_{\text{cell}}^{(2)}[q]+\mu\bar{n}\int q(r)d\mathbf{r}\\&=E_{\text{cell}}[\bar{n}]+F[q]\ ,\end{aligned}$$

where

$$\tilde{E}_{\text{cell}}^{(2)}[q]\equiv(5/9)(k\hbar^2/m_e)\bar{n}^{5/3}\int q^2(r)d\mathbf{r}-Ze^2\bar{n}\int[q(r)/r]d\mathbf{r}+e^2\bar{n}^2\int\int[q(r)/|\mathbf{r}-\mathbf{r}'|]d\mathbf{r}\,d\mathbf{r}'\ . \tag{6.22}$$

$E_{\text{cell}}[\bar{n}]$ comprises the kinetic-energy contribution and two potential-energy contributions already accounted for. Setting $\delta F[q]/\delta q=0$, we obtain, writing R_c for R_{cell},

$$(10/9)ka_0\bar{n}^{2/3}q(r)-(Z/r)+2\pi\bar{n}(R_c^2-\tfrac{1}{3}r^2)+(\mu/e^2)=0\ , \tag{6.23}$$

where we divided by $\bar{n}e^2$ and used

$$\int d\mathbf{r}'/|\mathbf{r}-\mathbf{r}'|=2\pi(R_c^2-\tfrac{1}{3}r^2)\ .$$

To evaluate μ, we integrate Eq. (6.23) over $d\mathbf{r}$ and use $\int q(r)d\mathbf{r}=0$ and (6.18).

We find that

$$\mu=(3/10)(Ze^2/R_c) \tag{6.24}$$

and therefore, from Eq. (6.23), that

$$\tfrac{10}{9}ka_0\bar{n}^{2/3}q(r)=Z\left[\frac{1}{r}+\frac{r^2}{2R_c^3}-\frac{9}{5R_c}\right]\ . \tag{6.25}$$

[$q(r)$ is clearly not small for small r, but the volume integral in $q(r)$ of the offending Z/r term and of the terms in Eq. (6.22) are perfectly well defined; without further justification, which should not be difficult to provide, we assume that it is legitimate to treat $q(r)$ as a perturbation.] With the $q(r)$ just obtained, we use the virial theorem in the form

$$\tilde{E}^{(2)}_{\text{cell}}[q]=-(5/9)(k\hbar^2/m_e)\bar{n}^{5/3}\int q^2(r)d\mathbf{r}$$

to obtain

$$E^{(2)}_{\text{cell}}=-\frac{324}{175}\left[\frac{4}{9\pi}\right]^{2/3}Z^{7/3}\ \text{Ry}\ . \tag{6.26}$$

[We used the fact that the virial theorem for the terms in Eq. (6.22) is of the usual form, that is, the total energy is the negative of the kinetic energy. The proof differs slightly from that given in Eqs. (5.10) and (5.11) for the Lenz energy functional. Thus, since $\int q(r)d\mathbf{r}=0$, one can introduce $q_s(r)=s^t q(sr)$, with t arbitrary; further, Eq. (6.22) contains $\bar{n}$, and under $r\to sr$ one has $\bar{n}\to s^3\bar{n}$.] It is interesting that for fixed $\bar{n}$ both the first- and second-order Coulomb corrections, the second and third terms in the expansion of the TF energy, can be obtained analytically. As expected, the ratio of $E^{(2)}_{\text{cell}}$ to $E^{(1)}_{\text{cell}}$, where $E^{(1)}_{\text{cell}}$ is defined by Eq. (6.17), is of the order of the expansion parameter p defined by Eq. (6.20). The value of $E^{(2)}_{\text{cell}}$ was first obtained by Salpeter (1961), who refers to it simply as the TF correction. Salpeter used TF theory in its differential equation form; here, as in many applications, the Lenz-energy-functional approach is not particularly simpler in terms of the calculation to be performed, but makes the direction along which to proceed almost obvious, requiring much less ingenuity. The straightforward rederivation above of $E^{(2)}_{\text{cell}}$ as an exercise in the use of the Lenz energy functional is due to R. Shakeshaft and the author (unpublished).

Salpeter's result is more accurate than that obtained in Eq. (6.26), since he used the relativistic form $(p^2c^2+m_e^2c^4)^{1/2}-m_ec^2$ for the kinetic energy rather than $p^2/2m_e$. One must be careful here. In studying the collapse condition of the white dwarf, it is reasonably clear that it is consistent to treat the kinetic energy relativistically and the (gravitational) potential energy nonrelativistically, for the former originates in the rapidly moving electrons while the latter originates in the slowly moving nuclei. In the present case, however, both the kinetic energy and the (Coulombic) potential energy originate in the rapidly moving electrons. Salpeter checked that the relativistic effects on the interaction are of higher order. He also studied a number of other effects that we have not considered at all.

F. Divergence of perturbation series in quantum electrodynamics

If all pair interactions have an attractive component, that component, even if relatively weak pairwise, can become dominant for a sufficiently large number N of particles. The energy of the ground state of the system can then increase faster than N as N increases, and this can lead to systems with very interesting physical properties. In neutron stars and white dwarfs, the always attractive component is the gravitational interaction. Coulomb interactions play a somewhat similar role in atoms of large Z. There the attractive electron-nucleus interaction dominates the repulsive e^-e^- interaction. Approximately, therefore, we have only attractive interactions, and the ground-state energy does increase faster than Z, namely, as $Z^{7/3}$. However, no atom can have a very large number of electrons, for the magnitude of Z is limited by the nature of the nuclear forces. There can be an arbitrarily large number of electrons in matter, but there the repulsive Coulomb interactions almost counteract the attractive ones. There is one (unphysical but nevertheless very interesting) case for which, with an arbitrarily large N, there is an attractive Coulomb interaction between each pair. It occurs in the study of the convergence of perturbation series in quantum electrodynamics. The charge e of the electron is the perturbation parameter, and, as in many convergence studies, one replaces functions of a real variable, here e, by functions of a complex variable, which we denote by e': the charge e' can be complex, and in particular it can be $\pm ie$. The nonrelativistic e^2/r_{12} interaction between a pair of like particles becomes $(e')^2/r_{12}$, which can assume the value $(\pm ie)^2/r_{12}$, that is, $-e^2/r_{12}$; the interaction is then attractive. Correspondingly, the interaction between a pair of unlike particles is then repulsive.

In a paper with the title almost the same as the heading of this subsection, Dyson (1952) used the above approach to argue that, for any physical quantity $F(e^2)$, a power series of the form obtained in perturbation theory,

$$F(e^2)=a_0+a_2e^2+a_4e^4+\cdots\ , \tag{6.27}$$

diverges. (Dyson noted that the argument is lacking in mathematical rigor and in physical precision, and intended it to be suggestive, but believed it to be convincing enough to merit publication.) The significance of the result is dramatized by the simplicity of the argument. The paper is two pages long and contains only two equations, Eq. (6.27) above and Eq. (6.28) below. Following Feynman (1949, 1950), Dyson took the interaction v between like charges to be given by

$$v=e^2\delta_+(s_{12}^2) , \tag{6.28}$$

where $s_{12}^2=c^2(t_1-t_2)^2-r_{12}^2$ is the square of the space-time interval between the charges and δ_+ is the Heisenberg delta function, a modification of the Dirac delta function. The properties of δ_+ need not concern us; for our purposes, the important property of v is that it is proportional to e^2, since it then follows that $F(e^2)$ will have the form given in Eq. (6.27) if calculated in perturbation theory. But if the expansion is to converge for the physical value of e^2, $F[(e')^2]$ must have a range of convergence at least equal to e^2, and, in particular, the expansion for $F(-e^2)$ must also converge. But $F(-e^2)$ can be reinterpreted as the value of the physical property for a fictitious world in which like particles attract and unlike particles repel. The "electrons" and "positrons" in that world have the pure imaginary charges $+ie$ and $-ie$, respectively—or vice versa. We define the energy of the vacuum in that fictitious world to be zero, and we show that there exist states of the same net charge (zero) as the vacuum, states which can therefore be coupled to the vacuum, with lower energy. The vacuum will therefore be unstable. (Arguments of this kind may or may not have some relevance to an understanding of the Big Bang.)

To study the stability of the vacuum, we consider states with N "electrons" in one region of space and N "positrons" in a distant region of space. The repulsion between each "electron" and each distant "positron" can then be neglected. We place each "electron" in its own sphere of radius $\overline{r}$, and the collection of the N "electron" spheres in a large sphere of radius $R\approx N^{1/3}\overline{r}$. We choose $\overline{r}$ to satisfy $\overline{r}\gg\hbar/m_ec$, so that it is consistent to calculate the kinetic energy of an "electron" nonrelativistically, for the nonrelativistic kinetic energy will be of the order of $\hbar^2/m_e\overline{r}^2$, much less than the rest energy m_ec^2. It is then also consistent to use the nonrelativistic Coulomb expression $-e^2/r_{12}$ for the interaction of a pair. Proceeding as usual, but including the rest energy of the "electrons," and expressing the result in terms of $\overline{r}$ rather than R, we find

$$\widetilde{E}(\overline{r})\approx Nm_ec^2+N(\hbar^2/m_e\overline{r}^2)-N^{5/3}(e^2/\overline{r}) . \tag{6.29}$$

A similar expression holds for the "positrons." We can of course give a more accurate TF estimate of $\widetilde{E}(\overline{r})$, but it will not be necessary. Since the attractive term has the strongest N dependence, it is clear that $\widetilde{E}(\overline{r})$ as given by Eq. (6.29)–or by a TF approximation or exactly—will have a range of negative values extending arbitrarily far down as N increases. The vacuum is therefore unstable. (States other than the vacuum, those containing a small number of *physical* electrons and positrons, can similarly be expected to be unstable. The state of large numbers of physical electrons and positrons has not been studied in the relativistic context, for that would require a many-body QED analysis. Though the argument may not require such an assumption, we shall simply assume that the energy of such a system increases less rapidly than the five-thirds power of the number of physical electrons and positrons; systems of large numbers of physical electrons and positrons will then also be unstable.) The spectrum of the Hamiltonian will therefore be quite different for $e^2>0$ and for $e^2<0$. This difference persists for any value of e, down to $e=0$. It is therefore to be expected that $F(-e^2)$ is not analytic, or equivalently that v cannot be treated as a perturbation and that the power-series expansion of $F(e^2)$ will diverge. There may of course be a nonperturbative formulation of quantum electrodynamics, but even the nonconvergent series in Eq. (6.27) can be expected to have a useful interpretation, for only the high-order terms in the expansion will be very big, and the leading terms should give a reasonable estimate of $F(e^2)$. There is therefore no contradiction between the extraordinary accuracy of perturbation-theoretic predictions of QED and the divergence of the perturbation series.

There are other ways of "understanding" the divergence. If the vacuum can decay, the energy of the vacuum has an imaginary component. But in any finite perturbation-theoretic calculation, the energy will be real. Alternatively, although the probability of decay of the fictitious vacuum into any particular state of "electrons" and "positrons" may be arbitrarily small, the fictitious vacuum is infinite, and one can expect that somewhere some state of "electrons" and "positrons" will appear instantaneously.

The above difficulty does not arise in nonrelativistic theory, even though there too the (static Coulomb) interaction is proportional to e^2, since nonrelativistic theory does not encompass positrons so that there are no states in the fictitious world that are of lower energy *and* that conserve charge. (There are of course perturbation series that diverge in nonrelativistic theory. An example is the Stark effect for an atom in an electric field $\mathbf{F}$. The spectrum is not analytic at $F=0$, for the spectrum of an atom in a field, no matter how weak, goes down to $-\infty$, or, alternatively, the energy of any state has an imaginary component, even when one turns off the radiation field, since any state can decay.)

We return now to the stability of the vacuum with respect to spontaneous pair production. Since $\hbar^2/m_e\overline{r}^2\ll m_ec^2$, we see that $\widetilde{E}(\overline{r})$ becomes zero, so that spontaneous pair production becomes possible, for

$$N\approx[m_ec^2/(e^2/\overline{r})]^{3/2}\gg(\hbar c/e^2)^{3/2}=(137)^{3/2}\gg1 .$$

One might object that for N that large a relativistic analysis might be demanded. That objection, however, cannot affect the argument that the vacuum is unstable—the argument was based on conditions under which the nonrelativistic approximation is valid—though it might reduce the value of N for which instability occurs. In fact it does not seem to do even that. Thus, adopting the ultrarelativistic limit and assuming that the Coulomb interaction remains valid, we find that the energy of N "electrons" confined to a sphere of radius R is

$$\tilde{E}_{\text{ultra}}(R)\approx\frac{N^{4/3}\hbar c-N^2e^2}{R}+Nm_ec^2 \ .$$

The lowest energy will then be positive for $N^{4/3}\hbar c>N^2e^2$, for any value of R, but for $N^{4/3}\hbar c<N^2e^2$ the lowest energy can be made negative by making R small. We therefore obtain the same value of N for which pair production is possible as that given by the nonrelativistic analysis.

VII. ATOMS AND POSITIVE IONS IN THE INTENSE MAGNETIC FIELD OF A NEUTRON STAR

We seek an estimate of the ground-state energy of a many-electron atom or positive ion in an intense uniform **B** field comparable in magnitude to those which almost surely exist at the surface of a neutron star, of the order of 10^{12} or 10^{13} G. To study this problem it will first be necessary to understand the "free-electron" problem of a single electron in an intense uniform **B** field but otherwise free. This "free-electron" problem was solved by Landau years ago. A proper discussion can be found in Landau and Lifshitz (1965), but a qualitative picture will suffice. Motion parallel to **B**, which we choose to be along the z axis so that $\mathbf{B}=B\hat{u}_z$, is unaffected by **B**, and the kinetic energy associated with motion along the z axis is arbitrary. Motion in the $\boldsymbol{\rho}=(\rho,\phi)$ plane perpendicular to **B** is defined by

$$\left[\frac{1}{2m_e}\left[\mathbf{p}_\perp-\frac{e\mathbf{A}}{c}\right]^2-E_\perp\right]\Psi_\perp(\boldsymbol{\rho})=0 \ , \tag{7.1}$$

where we can choose $\mathbf{A}(\boldsymbol{\rho})=-(B/2)(\boldsymbol{\rho}\times\hat{u}_z)$. It is convenient to introduce $\hat{\rho}$, $\mathbf{x}$, and $\psi(\mathbf{x})$, defined by

$$\hat{\rho}^2=(2\hbar c/eB),\quad \mathbf{x}\equiv\boldsymbol{\rho}/\hat{\rho},\quad \psi_\perp(\mathbf{x})=\Psi_\perp(\rho) \ . \tag{7.2}$$

$\hat{\rho}$ has the dimensions of length; it is *not* a unit vector. ($\hat{\rho}$ as a characteristic length for an electron in a uniform **B** field is a fairly standard notation. The reader is cautioned, however, that two definitions of $\hat{\rho}^2$, differing by a factor of 2, can be found in the literature. As in the use of both e^2/a_0 and $e^2/2a_0$ as the unit of energy in atomic physics, the use of slightly different definitions of $\hat{\rho}^2$ is ostensibly to breed a generation of careful, critical—and, somewhat unfortunately, mildly neurotic—physicists.) We now have

$$\{(-i\nabla_{\mathbf{x}}+\mathbf{x}\times\hat{u}_z)^2-[E_\perp/(\hbar^2/2m_e\hat{\rho}^2)]\}\psi_\perp(\mathbf{x})=0 \ . \tag{7.3}$$

$E_\perp$ is therefore proportional to $\hbar^2/(2m_e\hat{\rho}^2)$, with a proportionality constant of order unity for the ground state, and the dimension of the ground-state wave function will be of order $\hat{\rho}$. The argument depends upon the fact that x is dimensionless and that one cannot decouple motion in the ρ,ϕ plane into, for example, independent motions along x and y, respectively. [With $\mathbf{p}_\perp\to\mathbf{p}$, $\boldsymbol{\rho}\to\mathbf{r}$, $E_\perp\to E$, and $\psi_\perp(\boldsymbol{\rho})\to\psi(\mathbf{r})$, Eq. (7.1) defines motion perpendicular and parallel to **B**, and E the total energy. With **x** redefined as $\mathbf{x}\equiv\mathbf{r}/\hat{\rho}$, Eq. (7.3), with $E_\perp\to E$, is valid for a description of the full three-dimensional motion, but E is *not* simply proportional to $\hbar^2/m_e\hat{\rho}^2$; rather, it contains an additional term, the kinetic energy associated with motion parallel to **B**, a motion uncoupled to motion in the ρ,ϕ plane.]

It is useful to rewrite Eq. (7.2) in the dimensionless form of Eq. (7.3), but if one were only interested in obtaining $E_\perp$ to within a dimensionless constant of order unity one could simply note that e, B, and c enter only in the combination eB/c and then use dimensional analysis.

Since the electron can be bound to *any* **B** line, each energy level of an electron in a uniform **B** field is *infinitely* degenerate, adding a bit of spice to the problem. We also note that for $B=2.2\times10^{12}$ G, $\hat{\rho}$ is about $a_0/20$, and the ground-state energy is about 5 keV. The lowest excitation energy ΔE is somewhat larger, so that one must have exceedingly high temperatures before kT is of order ΔE. The energy required to flip the spin of the electron is also in the keV range.

A. The magnetic Lenz energy functional

1. A uniform number density

Turning now to the problem of interest, we have a system, in its ground state, consisting of N electrons and a nucleus of charge Ze, where $1\ll N\le Z$, in a uniform **B** field strong enough for the motion of an electron perpendicular to **B** to be practically unaffected by the electric field **E** generated by the nucleus and by the other electrons; motion parallel to **B** will of course be completely determined by **E**. To begin, we assume a uniform number density; more precisely, we assume that $n(\mathbf{r})=0$ far from the nucleus and $n(\mathbf{r})=n$, a constant, in some region whose shape is yet to be determined, near the nucleus. (The **E** field generated by the nucleus is spherically symmetric, while the **B** field is axially symmetric, so we expect to retain at least axial symmetry for the ground state.) To satisfy the Pauli principle, rigorously if somewhat crudely, we place *one* electron in each of a set of N nonoverlapping cylinders of radius $\hat{\rho}$ and length l, with the axes parallel to **B**; l is to be determined. (For sufficiently strong **B** fields, all electrons in the ground state will have the same spin projection.) The kinetic energy per electron in the plane perpendicular to **B** will be the same whether or not the electron is in an atom, and dropping both the total kinetic energy $E_{K\perp}$ associated with the perpendicular motion of the electrons and the energy E(spin) of the interaction of the electron spins with the **B** field merely redefines the zero-energy reference level. The kinetic energy per electron associated with motion parallel to **B** will be of the order of $\hbar^2/m_e l^2$, independent of the location of the cylinder (see Fig. 1). To maximize the attractive potential energy of the electron-nucleus interaction, we distribute the cylinders uniformly in a large sphere of radius R. (Thus, somewhat surprisingly, at least in our approximation the ground-state system is spherically symmetric even in the presence of the **B** field.) Volume considerations give $N\hat{\rho}^2 l \approx R^3$. The total kinetic energy associated with parallel motion is therefore

$$\widetilde{E}_{Kz}(R;B) \approx N(\hbar^2/m_e l^2) \approx N(\hbar^2/m_e)(N\hat{\rho}^2/R^3)^2 . \quad (7.4)$$

Proceeding as for the usual (laboratory) atom, we can approximate the many-body Hamiltonian $H(\mathbf{r}_1, \ldots, \mathbf{p}_N; B)$, in the presence of an intense uniform **B** field, with $E_{K\perp}$ and E(spin) subtracted, by

$$\widetilde{E}(R;B) = N^3\hbar^2\hat{\rho}^4/(m_e R^6) - (NZ - \tfrac{1}{2}N^2)e^2/R , \quad (7.5)$$

where the factor of 1/2 has been retained only to emphasize the fact that, as for laboratory atoms, $\widetilde{E}_{ee}$ is dominated by $\widetilde{E}_{e\nu}$ for $N \leq Z$, the domain of present interest. To simplify the algebra slightly, we now consider the neutral-atom case, $N = Z$. [It is quite trivial to obtain $R(B)$ and $E(B)$ for $N < Z$ as well.] Setting $d\widetilde{E}(R;B)/dR = 0$ and then substituting the value of R thereby obtained into Eq. (7.5) (with $N = Z$) gives

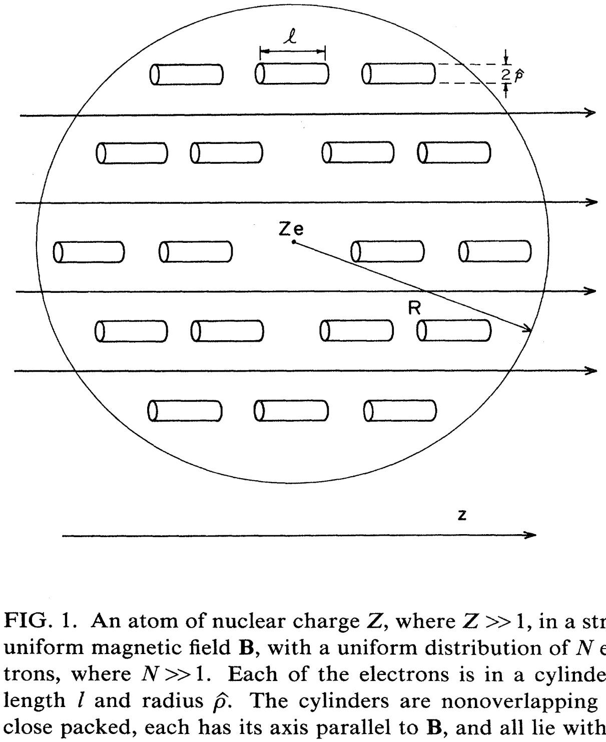

FIG. 1. An atom of nuclear charge Z, where $Z \gg 1$, in a strong uniform magnetic field **B**, with a uniform distribution of N electrons, where $N \gg 1$. Each of the electrons is in a cylinder of length l and radius $\hat{\rho}$. The cylinders are nonoverlapping and close packed, each has its axis parallel to **B**, and all lie within a sphere of radius R. Volume considerations give $N\hat{\rho}^2 l \approx R^3$.

$$R(B) \approx (Za_0\hat{\rho}^4)^{1/5}, \quad E(B) \approx -Z^{9/5}e^2/(a_0\hat{\rho}^4)^{1/5} . \quad (7.6a)$$

As opposed to the laboratory atom, an atom in an intense uniform **B** field is characterized by *two* lengths, a_0 and $\hat{\rho}$, and one *cannot* obtain the forms of $R(B)$ and of $E(B)$, even apart from the Z dependence, on dimensional grounds alone. Eliminating $\hat{\rho}$ in favor of B, we have

$$R(B) \approx (m_e a_0^2 c^2)^{1/5} Z^{1/5} B^{-2/5} ,$$
$$E(B) \approx -Z^2e^2/R(B) \approx -Z^{9/5}B^{2/5}e^2(m_e a_0^2 c^2)^{-1/5} . \quad (7.6b)$$

2. A variable number density

To allow for a variable number density, we note that for $n(r) = 0$ for $r > R$ and $n(r)$ a constant equal approximately to N/R^3 for $r < R$, the parallel kinetic energy per unit volume follows from Eq. (7.4) and is given by

$$\widetilde{E}_{Kz}(R;B)/\mathrm{Vol} \approx (\hbar^2\hat{\rho}^4/m_e)(N^3/R^9) \approx (\hbar^2\hat{\rho}^4/m_e)n^3 . \quad (7.7)$$

If therefore $n(r)$ is slowly varying, we write

$$\widetilde{E}_{Kz}[n;B] = (\pi^4/6)(\hbar^2\hat{\rho}^4/m_e)\int n^3(r)d\mathbf{r} . \quad (7.8)$$

We have inserted as a factor the constant $\pi^4/6$, the analog of the constant k in Eq. (4.9). To partially justify the insertion of this constant, we note that the electrons are tied to the magnetic field lines and that $\widetilde{E}_{Kz}[n;B]$ represents a one-dimensional kinetic energy which we have already evaluated. Thus, given a long cylinder of length L and radius $\hat{\rho}$ parallel to **B**, and having specified a constant number density n, we have as the number of electrons contained in the long cylinder $N_{\mathrm{cyl}} = n\pi\hat{\rho}^2 L$. We do *not* now put one electron in each small cylinder of length N_{cyl}/L, but rather use the last equation of Sec. V.A to obtain, as the exact expression, ignoring corrections of order $1/N_{\mathrm{cyl}}$,

$$\frac{\widetilde{E}_{Kz}[n;B]}{\mathrm{Vol}} = \frac{h^2 N_{\mathrm{cyl}}^3}{24 m_e L^2}\frac{1}{\pi\hat{\rho}^2 L} = \frac{\pi^4}{6}\frac{\hbar^2\hat{\rho}^4}{m_e}n^3 .$$

This does indeed differ from the approximate expression given in Eq. (7.7) by the factor $\pi^4/6$. The only point that remains to be justified is the use of $\hat{\rho}$, rather than $\hat{\rho}$ multiplied by a constant of order unity, for the radius of the cylinder. The justification begins with the realization that one set of solutions of the Schrödinger equation (7.1) for the infinitely degenerate ground state—excited states play no role for the strong **B** fields with their large energy separations and the relatively low kT values under consideration—is given by

$$\psi_m(\rho,\phi) = N_m(\rho/\hat{\rho})^{m} e^{-\rho^2/2\hat{\rho}^2} e^{im\phi}/\sqrt{2\pi} ,$$

with m the azimuthal quantum number. The value of the normalization constant N_m need not concern us. One immediately finds that the electron density $|\psi_m(\rho,\phi)|^2$ has its maximum value at $\rho_{m\ \max}=m^{1/2}\hat{\rho}$, with the relative width of the peak decreasing with m. For large m, the electron can therefore be allotted an area in the ρ,ϕ plane of $\pi(\rho_{m+1\ \max}^2-\rho_{m\ \max}^2)$ or $\pi\hat{\rho}^2$. Alternatively, each electron can be allotted its own small cylinder, of area $\pi\hat{\rho}^2$.

The "magnetic Lenz energy functional" is therefore given by Eqs. (4.9), with $\tilde{E}_K[n]$ of Eq. (4.9b) replaced by $\tilde{E}_{Kz}[n;B]$ of Eq. (7.8). The differential equation for the neutral atom, that is, the "magnetic TF differential equation," follows readily, and has been obtained, and it would be straightforward to obtain the differential equation for a positive ion.

The magnetic TF differential equation was first derived by Kadomtsev (1970). The magnetic Lenz energy functional was obtained by Mueller, Rau, and Spruch (1971); the latter paper includes a study of the relative magnitudes of the kinetic energy and of the e^-e^- and e^--nuclear potential energies, to be discussed in the following subsection. Both papers include efforts to define the domain of validity of magnetic TF theory. The **B** field must of course be strong enough to cause motion in the perpendicular plane to be largely unaffected by Coulomb interactions. On the other hand, if the **B** field is "ultrastrong," the strong state will be one in which each e^- is in a long cylinder of its own, the associated wave function will have no nodes with respect to the z coordinate, and a statistical theory will not be possible. (A wave function must have a fair number of nodes if the associated momentum is to be reasonably well defined.) An (analytic) attempt to go beyond magnetic TF theory, in the domain where magnetic TF theory is reasonably accurate, was made by Rau, Mueller, and Spruch (1975). Motivated by his interest in neutron stars, M. Ruderman provided much of the leadership in studies of systems in strong **B** fields. These systems include hydrogen atoms and iron atoms. In the latter case, one is interested not so much in the total energy of the ground state as in the much more difficult problem of the ionization energy, and numerical work is required. Furthermore, it is not clear for atoms in strong **B** fields, as it is for laboratory atoms, that the additional energy of binding associated with the formation of molecules is very small compared to atomic binding energies; atoms might therefore form strongly bound long chains in strong **B** fields and, if so, these one-dimensional chains could bind one another. A considerable computational effort has gone into the study of systems of large numbers of Fe atoms in strong **B** fields. Neuhauser, Koonin, and Langanke (1987) find that molecular chains will not form for $Z>2$ for $B>10^{12}$ G, nor for $Z>4$ for $B>5\times10^{12}$ G; if matter on the surface of a neutron star is bound at all, it is bound very weakly. This is understandable in that all spins are parallel, demanding a totally antisymmetric spatial wave function and thereby disallowing the predominant (spin-singlet) zero-field bonding mechanism. These authors also obtain (total) atomic binding energies, energies which satisfy the Z and B dependences of Eq. (7.6b), and the virial relation of Eq. (7.9), just below, rather well (see Chen and Spruch, 1987).

Reviews of some related matters include those of Ruderman (1974), Garstang (1977), and Canuto and Ventura (1977).

B. Relations among the three contributions to the energy

1. The ratio of the total kinetic energy E_{Kz} to the total potential energy E_V

When Eqs. (3.15) and (3.16) are used, it follows from the *form* of Eq. (7.5), that is, simply from the R^{-6} and R^{-1} dependences of the kinetic and potential energies, independent of the values of the numerical coefficients, that

$$6E_{Kz}+E_V=0\ . \tag{7.9}$$

We seek further physical insight into the origin of this equation. For a laboratory atom or positive ion, we have the virial theorem in its usual form, $2E_K+K_V=0$. If the electrons in the system have a velocity distribution that is spherically symmetric at each point **r**, E_K is three times the kinetic energy associated with a motion along any axis and in particular with motion along the z axis, and the virial theorem becomes $6E_{Kz}+E_V=0$, which is of the same form as Eq. (7.9). However, the electron velocities at any point for an atom or positive ion in a strong **B** field are *not* spherically symmetric, for the velocities perpendicular to **B** are very much larger than velocities parallel to **B**, and it is accidental that one obtains the appropriate form of the virial theorem by assuming a spherically symmetric velocity distribution. The correct approach is to consider directly the velocities parallel to **B**. We now do so, but to simplify the discussion we study the problem classically. (In our considerations just above of the velocity distribution at a point we were already thinking classically.) We let $\langle\ \rangle$ denote a time average, and f_{zi} the zth component of the force on the ith electron, and start from $f_{zi}=m_e d^2z_i/dt^2$. We can then write

$$\left\langle \sum_i z_i f_{zi} \right\rangle = \left\langle m_e \sum_i z_i \frac{d^2 z_i}{dt^2} \right\rangle = -2\left\langle \sum_i \frac{m_e}{2}\left[\frac{dz_i}{dt}\right]^2 \right\rangle = -2E_{Kz}\ ; \tag{7.9$'$}$$

in the penultimate step, we recognized, in close analogy to the argument used in the usual development of the virial theorem, that for a system of bound particles

$$\left\langle \sum_i m_e \frac{d}{dt}\left[z_i \frac{dz_i}{dt}\right] \right\rangle = 0\ .$$

f_{zi} is independent of $\mathbf{B}=B\hat{u}_z$. Proceeding along the same lines as for a laboratory atom, we find, inserting the z components of the Coulomb forces in Eq. (7.9′),

$$-2E_{Kz}=\left\langle \sum_i -\frac{Ze^2}{r_i}\frac{z_i^2}{r_i^2}\right\rangle+\left\langle \sum_{\text{pairs}} \frac{e^2}{r_{ij}}\frac{(z_i-z_j)^2}{r_{ij}^2}\right\rangle .$$

If the particles have a spherically symmetric *spatial* distribution, we can replace both z_i^2/r_i^2 and $(z_i-z_j)^2/r_{ij}^2$ by $\frac{1}{3}$, and we obtain

$$-2E_{Kz}=\tfrac{1}{3}(E_{e\nu}+E_{ee})=\tfrac{1}{3}E_V ,$$

which is just Eq. (7.9). The essential point is that, in the domain of B of interest, the atom or positive ion has lost spherical symmetry at each point $\mathbf{r}$ of the velocity distribution of the electrons, but the spherical symmetry of the spatial distribution of the electrons with respect to the origin has not been destroyed.

Although the numerical values of E_{Kz} and E_V are changed when one goes from Eq. (7.5) for $\tilde{E}(R;B)$ to the somewhat more precise magnetic Lenz energy functional, $\tilde{E}(R;B)$, Eq. (7.9) remains valid. The proof is identical in form to that used in Sec. V.B.2 for laboratory atoms. Introducing the scaled number density defined by Eq. (5.10), one finds $\tilde{E}_K[n_s;B]=s^6\tilde{E}_K[n;B]$, and Eq. (7.9) follows immediately.

2. The ratio of the electron-nucleus and electron-electron potential energies, $E_{e\nu}$ and E_{ee}

We turn now to the more interesting question of the ratio of the electron-nuclear contribution to the energy to the electron-electron contribution. We restrict our attention to the neutral-atom case. We can then readily obtain the magnetic TF differential equation for $n(r)$ and proceed formally, as in the derivation leading to Eq. (5.13), to obtain

$$-E_{e\nu}/E_{ee}=3 . \tag{7.10}$$

A simpler and more interesting derivation is one that is similar to the derivation of Rau for the laboratory atom, which led to Eq. (5.15a). We begin with Eq. (7.5) and insert coefficients c', $\tilde{c}$, and $\bar{c}$, obtaining a new expression for $\tilde{E}(R;B)$, an expression which differs from Eq. (5.14) only in the first term. [We absorb the factor $\frac{1}{2}$ in Eq. (7.5) into $\bar{c}$.] We minimize the new expression for $\tilde{E}(R;B)$ with respect to R, obtaining an energy $E(B)$, or, to be more explicit, $E(B,N,Z)$. As for the laboratory atom, we *assume* that, for fixed $Z,E(B)$ takes on its minimum value at $N=Z$ (or in the immediate neighborhood of $N=Z$). This assumption is valid in the magnetic TF approximation, an approximation we are not now making, and it is the only aspect of magnetic TF theory we shall need. Setting $dE(B,N,Z)/dN=0$ at $N=Z$ gives $\tilde{c}=3\bar{c}$, which is the same result as that contained in Eq. (7.10). Equations (7.9) and (7.10) give

$$E_{Kz}:-E_{e\nu}:E_{ee}=1:9:3 . \tag{7.11}$$

It is interesting to compare the ratio of $-E_{e\nu}$ to E_{ee} for the three cases for which we have obtained the ratio [see Eqs. (5.13), (7.10), and (6.16)]:

(α) neutral laboratory atom: $-E_{e\nu}/E_{ee}=7$;

(β) neutral atom in intense **B** field: $-E_{e\nu}/E_{ee}=3$;

(γ) neutral "highly compressed" atom: $-E_{e\nu}/E_{ee}=2$.

We are concerned with the ground state (and with $Z\sim\infty$), and the electrons will therefore organize themselves to give the lowest possible energy. As the extent to which the nucleus "controls" the motion of the electrons increases, the nonuniformity of the distribution should increase, and, in line with the discussion at the very end of Sec. V.B.2, we can expect the ratio of $-E_{e\nu}$ to E_{ee} to increase as well. This is in agreement with the results for the ratios just quoted. For the laboratory atom, the e^--nuclear interactions influence electronic motions in all directions; for an atom in an intense **B** field the influence is exerted only on electronic motions parallel to **B**; and for "highly compressed" atoms, as in white dwarfs, the distribution of the e^-'s to lowest order is uniform, unaffected by the interactions with the nucleus.

VIII. THE STABILITY OF BULK MATTER

A. Teller's no-binding theorem for molecules

Since TF theory leads so simply to some very interesting information on atoms, it is natural to attempt to extend the TF approach to the study of molecules. We ignore the kinetic energy $E_{k,\text{nuc}}$ of the nuclei, not only because $E_{k,\text{nuc}}$ will be small but because we shall be interested primarily in a lower bound on the ground-state energy of the molecule, and the inclusion of $E_{K,\text{nuc}}$ can only (slightly) raise the ground-state energy. To simplify the discussion we assume that there are N_ν nuclei, each of charge Ze, with (fixed) coordinates R_μ, $1\le\mu\le N_\nu$; we further assume charge neutrality, so that, with N_e the number of electrons, we have $N_e=ZN_\nu$. (In the atomic case, where the only particle number of interest was the number of electrons, we wrote N for the number of electrons.) Our Lenz energy functional for a molecule is then

$$\tilde{E}'_{\text{TF}}[n]=\tilde{E}_K[n]+\tilde{E}'_{e\nu}[n]+\tilde{E}_{ee}[n]+E_{\nu\nu} . \tag{8.1a}$$

Primes have been used, where necessary, to distinguish between molecular and atomic energies. Thus $\tilde{E}_K[n]$ and $\tilde{E}_{ee}[n]$ are of the same form as for an atom, and are given by Eqs. (4.9b), (4.9d), and (4.9g). $\tilde{E}'_{e\nu}[n]$ is now a sum of terms,

$$\tilde{E}'_{e\nu}[n]=-Ze^2\sum_{\mu=1}^{N_\nu}\int\frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_\mu|}d^3r , \tag{8.1b}$$

and a term to represent the interaction energy of the nuclei a function, not a functional,

$$E_{\nu\nu}=\frac{Z^2e^2}{2}\sum_{1\le\mu\neq\tau\le N_\nu}\sum\frac{1}{|\mathbf{R}_\mu-\mathbf{R}_\tau|} , \tag{8.1c}$$

has been added. Teller (1962) showed that in the TF model the ground state was that state in which all nuclear separations were infinite, with the associated energy the sum of the isolated atomic TF energies, that is,

$$\tilde{E}'_{\rm TF}[n] \geq N_\nu E_{\rm TF} = -N_\nu c_7 Z^{7/3}\ {\rm Ry}\ , \tag{8.2}$$

where c_7 is given in Eq. (5.9) and where we are here using $E_{\rm TF}$ rather than simply E. We shall not give the proof, but a few remarks about the result and the proof are in order.

(i) The result was suggested by TF numerical molecular calculations (Sheldon, 1955), which failed to provide binding, that is, to generate a total energy of the molecule below that of the sum of the isolated atomic energies. The result is not remarkable and might perhaps have been suggested by the following consideration: if the TF model had given molecular binding, the results would have been grossly in error, for TF energies scale as $Z^{7/3}$ and TF distances scale as $Z^{-1/3}$, whereas molecular binding energies and distances are roughly independent of Z. Thomas-Fermi theory gives the exact energy of an atom as $Z \sim \infty$—more precisely the fractional error~ 0—because the fraction of electrons not handled correctly, those in regions where the potential is not sufficiently slowly varying, becomes vanishingly small as $Z \sim \infty$. However, that vanishing fraction includes not only the innermost electrons—which, as shown in Sec. IX.B, give the leading correction to $E_{\rm TF}$—but the outermost electrons, which are largely responsible for molecular binding.

(ii) If the result itself is not remarkable, the fact that one can prove such a result under such general circumstances is remarkable. Teller's proof is a very clever one, involving a fair amount of chitchat but almost no mathematics, but the proof is not without weaknesses. First, it assumes that one is free to move about arbitrarily small charges, smaller than that of the electron. Second, to avoid singularities, the nucleus is not taken to be a point charge but is given structure, yet nuclear forces are never introduced. A rigorous proof was given by Lieb and Simon (1973, 1977).

(iii) The date of the proof, 1962, is not too flattering to our profession. The proof was given 35 years after the TF papers.

The reader might wonder why a major failure of the TF model should be given much emphasis. We will shortly see that that major failure was turned into a stunningly simple proof of perhaps the most important property of bulk matter, its stability.

B. Proof of the stability of bulk matter

By the stability of an atom one simply means that the ground-state energy is bounded from below. By the stability of bulk matter one means much more, namely, that for a system containing a total of N_e electrons it is possible to obtain a lower bound on the ground-state energy $E'(N_e)$ which is linear in N_e, that is,

$$E'(N_e) \geq -AN_e\ {\rm Ry}\ , \tag{8.3}$$

with A a constant. (It would make little difference for present purposes if we replaced N_e by $N_e + N_\nu$.) This property is essential if matter is to have intrinsic properties, that is, if, for example, the conductivity of a piece of copper is to be independent of its mass. That matter has intrinsic properties is so well known that it seems obvious, but it was first proved in the 1960s! The stability of matter is one of the very many important properties that classical physicists at the turn of the last century could not have proved when some were saying that all that was left in physics was to obtain more significant figures. (It is unnerving to try to imagine what physicists 90 years hence will think of some of the things being said today.) They could not have begun to prove the result for it depends upon the fact that the electron is a fermion.

Before giving a formal proof of the stability of matter, we note that a remarkably simple-looking theorem of Onsager makes the stability as defined by Eq. (8.3) rather reasonable. Consider P particles at rest at locations $\mathbf{r}_i$, with charges e_i. The theorem states that the potential energy V of the system satisfies

$$V = \tfrac{1}{2} \sum\sum_{1 \leq i \neq j \leq P} \frac{e_i e_j}{r_{ij}} \geq -\sum_{i=1}^{P} \frac{e_i^2}{R_i^*}\ ,$$

where R_i^* is the distance from the ith particle to its nearest neighbor. In other words, no matter how one arranges the particles, V of the system is saturated, that is, is bounded from below by the potential energy of a system of P particles in which each particle interacts *with one and only one other particle,* a particle of charge equal and opposite to its own and located at the position, in the original system, of its nearest neighbor. It is the single-sum bound on (the double sum) V which leads to a linear bound on V and therefore on the total energy of the original system.

The proof of Onsager's theorem, as given by Dyson (1968), is trivial; it is a statement in classical electrostatics. Draw a sphere of radius $(1/2)R_i^*$ about the ith particle, centered on the particle, and distribute the charge e_i uniformly on the sphere. Do this for each particle. Since $(1/2)R_i^* + (1/2)R_j^* \leq r_{ij}$, the spheres do not intersect. The total electrostatic energy E_T of the charged spheres is therefore

$$E_T = \sum_{i=1}^{P} \frac{e_i^2}{2(R_i^*/2)} + V\ ,$$

where the first term is the sum of the self-energies of the spheres. Since any total electrostatic energy is positive, the theorem follows.

We turn now to the formal proof of the stability of bulk matter. To simplify the discussion we again assume the matter to be neutral and each of the N_ν nuclei to have the same atomic number Z. Since the energies with which atoms bind to form molecules are small compared to the sum of the binding energies of the atoms, we expect $E'(N_e)/\mathrm{Ry}$ to be of the order of $-N_\nu Z^{7/3}$, that is, $-N_e Z^{4/3}$. A in Eq. (8.3) is Z dependent; for $Z=1$, we have $N_\nu = N_e$, and $E'(N_e)$ will be of the order of $-N_e\mathrm{Ry}$; one then expects the constant A in Eq. (8.3) to be of order unity. As noted previously, Dyson and Lenard (Dyson, 1967; Dyson and Lenard, 1968; Lenard and Dyson, 1968) first proved the existence of an inequality of the form (8.3). The result is *exceptionally* notable, but the proof is an extremely difficult one and the constant A obtained was of the order of 10^{14}. (Dyson has stated in print that he is not the deep creative thinker Oppenheimer had hoped for when Dyson was hired by the Institute for Advanced Study, but only a problem solver. One hesitates to disagree with Dyson, but the facts are quite to the contrary.) A very much simpler proof was provided by Lieb and Thirring (1975) in one of the most beautiful papers it has ever been my pleasure to read; they also reduced the value of A to of order 10. A more detailed discussion is given in Lieb (1976). An essential element in the proof is Teller's no-binding theorem. That this theorem should prove useful in the proof is not, after all, that surprising. Thus a molecular physicist will find TF theory useless, but, in fact, the no-binding theorem is a very useful result if one is interested in the leading term in the total energy $E'(N_e)$. In fact, the leading term in $E'(N_e)$ is $N_\nu E_{\mathrm{atom}}$, where E_{atom} is the exact energy of an isolated atom, while TF theory gives $N_\nu E_{\mathrm{TF}}$ as its estimate of $E'(N_e)$. Thus TF theory not only gives an estimate of the desired form, linear in N_ν and therefore in N_e, but is even moderately accurate, the more so for Z large.

To begin the proof of stability we introduce the wave function $\psi(\mathbf{r}_1,\ldots,\mathbf{r}_{N_e})$, which is antisymmetric in the electron coordinates—the spin dependence has been suppressed—and normalized to unity, but is otherwise arbitrary. We then consider the functional

$$\tilde{E}[\psi] \equiv (\psi, H\psi) = \tilde{E}_K[\psi] + \tilde{E}_{e\nu}[\psi] + \tilde{E}_{ee}[\psi] + E_{\nu\nu} , \tag{8.4a}$$

where H is the full quantum-mechanical Hamiltonian, where the subscripts have their usual connotations, and where, with spin summations understood,

$$\tilde{E}_K[\psi] = \sum_{i=1}^{N_e} \frac{\hbar^2}{2m_e} \int |\nabla_i \psi|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} , \tag{8.4b}$$

$$\tilde{E}_{e\nu}[\psi] = -Ze^2 \sum_{\mu=1}^{N_\nu} \sum_{i=1}^{N_e} \int \frac{|\psi|^2}{|\mathbf{r}_i - \mathbf{R}_\mu|} d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} , \tag{8.4c}$$

and

$$\tilde{E}_{ee}[\psi] = \frac{e^2}{2} \sum\sum_{1 \le i \ne j \le N_e} \int \frac{|\psi|^2}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e} . \tag{8.4d}$$

$E_{\nu\nu}$ is given by Eq. (8.1c). The proof consists in showing that $\tilde{E}[\psi] \ge -\mathrm{const}\ N_e\mathrm{Ry}$ for any ψ, and therefore for the true wave function, so that $E'(N_e) \ge -\mathrm{const}\ N_e\mathrm{Ry}$, where $E'(N_e)$ is the true ground-state energy. The approach used in bounding $\tilde{E}[\psi]$ is to first bound each of the ψ-dependent functionals in Eq. (8.4a) by n-dependent functionals, where the one-body function $n(\mathbf{r})$ is obtained from ψ in the usual way, that is,

$$n(\mathbf{r}) = N_e \int |\psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_{N_e})|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_{N_e} , \tag{8.5}$$

with summation over spins understood; as required, the $n(\mathbf{r})$ so defined satisfies $\int n(\mathbf{r})d\mathbf{r} = N_e$. The no-binding theorem will be used to obtain a bound on $\tilde{E}_{ee}[\psi]$ of the desired form, and then again to bound a sum of n-dependent functionals.

$E_{\nu\nu}$ is independent of ψ and can be left as is. Since the operator appearing in Eq. (8.4c) for $\tilde{E}_{e\nu}[\psi]$ is a sum of one-body operators, we can write

$$\tilde{E}_{e\nu}[\psi] = -Ze^2 \sum_{\mu=1}^{N_\nu} \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_\mu|} d^3r = \tilde{E}'_{e\nu}[n] , \tag{8.6}$$

using Eq. (8.1b). Lieb and Thirring (1975) bound $\tilde{E}_K[\psi]$ by an extension of the one-body Sobolov inequality, Eqs. (3.5) and (3.6), obtaining

$$\tilde{E}_K[\psi] \ge c_K \tilde{E}_K[n] , \tag{8.7}$$

with c_K a known number somewhat less than unity, and the authors surmise that the inequality remains valid for $c_K = 1$. That an inequality of the form (8.7) exists, and that it might be valid even for $c_K = 1$, is not unexpected, for $\tilde{E}_K[n]$ was obtained assuming free electrons, or, equivalently, noninteracting electrons in a constant potential, and any variation in the potential can be expected to increase the kinetic energy. We shall discuss the proof of Eq. (8.7), with $c_K = (4\pi)^{-2/3}$, in Appendix C; we also show there that $c_K \le 1$.

The remaining ψ-dependent functional $\tilde{E}_{ee}[\psi]$ contains a sum of *two-body* operators and is therefore difficult to bound by a functional of n. It can be done, however; the method is imaginative enough to bring pleasure to even a jaded theorist's heart. The proof of the no-binding theorem did not in any way depend upon the mass m_e of the electron, and remains valid for fermions of mass $m = m_e/\gamma$, for $\gamma > 0$, and, as a tool in the analysis, we consider such fermions. Since $\tilde{E}_K[n] \propto 1/m_e$, while $\mathrm{Ry} \propto m_e$, the theorem can be written as

$$\gamma \tilde{E}_K[n] + \tilde{E}'_{e\nu}[n] + \tilde{E}_{ee}[n] + E_{\nu\nu} \ge N_\nu E_{\mathrm{TF}}/\gamma , \tag{8.8}$$

with the terms defined by Eqs. (4.9b), (8.6), (4.9d), (8.1c), and (5.9), respectively. The clever move, which might remind one of some brilliant castling move by Bobby Fisher in his prime, is to reinterpret the nuclear coordinates as electron coordinates, a move which is possible only if there are as many nuclei as there are electrons. We can arrange to have $N_e = N_\nu$ by choosing $Z=1$, that is, by considering a system with N_e electrons, as in the system under consideration, but with N_e protons rather than with N_e/Z nuclei of charge Z. Changing variables from μ to i and from ν to j, with the reinterpretation yet to be made, Eq. (8.8) then becomes

$$\gamma\tilde{E}_K[n]-e^2\sum_{i=1}^{N_e}\int\frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_i|}d\mathbf{r}+\tilde{E}_{ee}[n]+\frac{e^2}{2}\sum\sum_{1\le i\ne j\le N_e}\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|}\ge N_eE_{\mathrm{TF}}/(\gamma Z^{7/3})\ , \tag{8.9}$$

with E_{TF} that for the original nuclei and with $E_{\mathrm{TF}}/Z^{7/3}$ to be interpreted as a TF estimate of the energy of a hydrogen atom. [The inequality is valid for any $n(\mathbf{r})$ and therefore for any ψ, including any ψ considered in the study of nuclei of charge Z.] The coordinates $\mathbf{R}_i$ and $\mathbf{R}_j$ are arbitrary numbers and can be reinterpreted as the electron coordinates $\mathbf{r}_i$ and $\mathbf{r}_j$. We make that reinterpretation, multiply by $|\psi|^2$, and integrate over the space and spin coordinates of the electrons. The terms in Eq. (8.9) independent of $\mathbf{R}_i$ and $\mathbf{R}_j$ are unaffected. Since $1/|\mathbf{r}-\mathbf{R}_i|\to 1/|\mathbf{r}-\mathbf{r}_i|$ is a one-body operator, we have

$$\sum_{i=1}^{N_e}\int\frac{|\psi|^2}{|\mathbf{r}-\mathbf{r}_i|}d\mathbf{r}_1\cdots d\mathbf{r}_{N_e}=\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\ ,$$

and, therefore,

$$-e^2\sum_{i=1}^{N_e}\int d\mathbf{r}\,n(\mathbf{r})\int\frac{|\psi|^2}{|\mathbf{r}-\mathbf{r}_i|}d\mathbf{r}_1\cdots d\mathbf{r}_{N_e}=-2\tilde{E}_{ee}[n]\ . \tag{8.10}$$

On integrating over $|\psi|^2$, the $1/|\mathbf{R}_i-\mathbf{R}_j|\to 1/|\mathbf{r}_i-\mathbf{r}_j|$ term becomes the term of interest, $\tilde{E}_{ee}[\psi]$, and, using Eq. (8.10), we obtain from the inequality (8.9) a bound of the desired (n-dependent) form,

$$\tilde{E}_{ee}[\psi]\ge\tilde{E}_{ee}[n]-\gamma\tilde{E}_K[n]+N_eE_{\mathrm{TF}}/(\gamma Z^{7/3})\ . \tag{8.11}$$

When used in Eq. (8.4a), Eq. (8.6) and inequalities (8.7) and (8.11) give

$$\tilde{E}[\psi]\ge\{(c_K-\gamma)\tilde{E}_K[n]+\tilde{E}'_{e\nu}[n]+\tilde{E}_{ee}[n]+E_{\nu\nu}\}$$
$$+N_eE_{\mathrm{TF}}/(\gamma Z^{7/3})\ . \tag{8.12}$$

The expression in curly brackets in Eq. (8.12) is the Lenz energy functional for $N_e=ZN_\nu$ fermions of mass $m_e/(c_K-\gamma)$—we therefore impose the restriction $\gamma<c_K$, so that, since $c_K\le 1$, these fermions have a mass greater than that of an electron—and N_ν nuclei each of charge Z so that, by the no-binding theorem, we have, for the { } in Eq. (8.12),

$$\{\ \}\ge N_\nu E_{\mathrm{TF}}(c_K-\gamma)^{-1}\ ,$$

and, therefore,

$$\tilde{E}[\psi]\ge N_\nu E_{\mathrm{TF}}[(c_K-\gamma)^{-1}+(\gamma Z^{4/3})^{-1}]\ .$$

The γ that minimizes $\tilde{E}[\psi]$ is

$$\gamma=c_K(1+Z^{2/3})^{-1}\ ,$$

which, as required, is less than c_K. The bound on $\tilde{E}[\psi]$, and therefore on $E(N_e)$, reduces to

$$E[N_e]\ge -N_\nu|E_{\mathrm{TF}}|(1+Z^{-2/3})^2/c_K\ , \tag{8.13}$$

which proves the stability of matter.

For $Z\sim\infty$, the lower bound in Eq. (8.13) reduces to $N_\nu E_{\mathrm{atom}}/c_K$, which, apart from the $1/c_K$ factor, is the leading term in $E[N_e]$. [The value $c_K=(4\pi)^{-2/3}$ cited below Eq. (8.7) was improved to roughly $1.5\times(4\pi)^{-2/3}$ (Lieb, 1980) and has recently been improved further, by some 10% (Martin, 1989).] As noted above, the no-binding theorem, used in the proof, gives the leading term in the total energy exactly for $Z\sim\infty$, consistent with the result just quoted. Note that $\tilde{E}_{ee}[\psi]$, which includes direct and exchange contributions, is bounded by an expression, (8.11), that does not contain any exchange contributions. This too should not be too surprising, since $\tilde{E}_{ee}[\psi]$ is of the order of $Z^{7/3}$, while exchange effects are only of the order of $Z^{5/3}$ (see Sec. X.A). In fact, since $\tilde{E}_{ee}[n]$, $\tilde{E}_K[n]$, and $N_\nu|E_{\mathrm{TF}}|$ are comparable for good approximations ψ and therefore n, and since $\gamma\propto Z^{-2/3}$ for $Z\gg 1$, the lower bound (8.11) on $\tilde{E}_{ee}[\psi]$, ignoring terms of order $Z^{-2/3}$, is $\tilde{E}_{ee}[n]$, an excellent approximation.

Apart from its use in stability studies, the inequality (8.11) provides an interesting bound on $\tilde{E}_{ee}[\psi]$ itself. The minimizing γ is now

$$\gamma=(Z^{7/3}\tilde{E}_K[n]/N_e|E_{\mathrm{TF}}|)^{-1/2}\ ,$$

which gives

$$\tilde{E}_{ee}[\psi]-\tilde{E}_{ee}[n]\ge -2[\tilde{E}_K[n]N_e|E_{\mathrm{TF}}|/Z^{7/3}]^{1/2}\ . \tag{8.14}$$

The lower bound involves $\int n^{5/3}(\mathbf{r})d\mathbf{r}$. A more interesting lower bound on the difference defined by Eq. (8.14), the "indirect Coulomb energy," one which involves $\int n^{4/3}(\mathbf{r})d\mathbf{r}$, the form expected for exchange effects, has been obtained by different methods (Lieb, 1979).

In the above discussion, we assumed that the system was neutral and that all nuclei had the same charge. It is trivial to eliminate those assumptions. A more interesting point is the extension of the above results to bosons. To make that extension, we consider "electrons" with spin s and with $q=2s+1$ projections, as opposed to the two projections for the electron. In Eq. (4.11) relating $p_F(\mathbf{r})$ and $n(\mathbf{r})$, we must therefore insert a factor of $q/2$ on the left-hand side. In Eq. (4.9b) for $\tilde{E}_K[n]$, one must therefore multiply by $q/2$, to account for the different number of projections; one must also divide by $(q/2)^{5/3}$, to account for the new relation that arises on expressing $p_F^5(\mathbf{r})$ in terms of $n(\mathbf{r})$. The net effect is that $\tilde{E}_K[n]$ is changed by the factor $(q/2)^{-2/3}$, which is equivalent to having "electrons" of mass $(q/2)^{2/3}m_e$. The bound on $E(N_e)$ in Eq. (8.13) is therefore to be multiplied by $(q/2)^{2/3}$. To consider bosons we need merely set $q=N_e$, since all of the "electrons" can then be accommodated in the same state. We thereby arrive at

$$E(N_e;\text{bosons}) \geq -ZN_e^{5/3}|E_{\text{TF}}|(1+Z^{-2/3})^2/(2^{2/3}c_K)\ ,$$

so that stability does not follow. A lower bound with an $N_e^{5/3}$ factor was first obtained by Dyson and Lenard (1967, 1968), and Dyson (1967) obtained an upper bound with an $N_e^{7/5}$ form. It follows that a system of nuclei and "bosonic electrons," where the bosons interact via Coulomb forces only, is not stable, and, as Dyson (1967) pointed out, no such bosons are known. See also Dyson (1968). Conlon, Lieb, and Yau (1988) have shown that the correct power law is $N_e^{7/5}$.

Returning to ordinary matter, we note that the review by Lieb (1976) contains many many theorems not discussed here, including, for example, a proof that the radius of a system containing N_e electrons is, as expected, at least of the order of $N_e^{1/3}$.

IX. A FIRST STEP BEYOND THOMAS-FERMI: THE SCOTT INNER-ELECTRON Z^2 CORRECTION

We now consider some improvements that have been made upon TF theory, restricting ourselves to atoms, and unless otherwise noted to neutral atoms. Further, we consider only the question of the total energy of the atom, but the path to a better estimate of the total energy leads simultaneously to a better estimate of the number density $n(r)$ and therefore to better estimates of the many quantities that can be expressed in terms of $n(r)$. We make a brief remark on notation. In previous sections, where TF estimates were the only estimates considered, it was normally unnecessary to append subscripts TF. We do so now to distinguish TF estimates from other estimates and from the true values.

A. The accuracy of the TF energy estimate

Before attempting to go beyond TF theory, it is natural to ask about the accuracy to be expected of the TF result, Eq. (5.9c),

$$E_{\text{TF}} = -c_7 Z^{7/3}\ \text{Ry}\ .$$

Since this result is based on a (semiclassical) statistical theory, it can be expected to improve in accuracy as Z, the number of electrons, increases. Is E_{TF} exact in the limit $Z \sim \infty$, that is, with E the true total energy of the atom, is the assertion that

$$(E - E_{\text{TF}})/E \sim 0 \quad \text{as } Z \sim \infty$$

correct? We begin with a qualitative discussion of this question and then cite some rigorous results that have been obtained.

Thomas-Fermi theory involves two primary approximations. First, the theory neglects exchange, but the exchange contribution is known to be of the order of $Z^{5/3}$, as shown by Dirac (1930) and discussed below in Sec. X.A. Second, it is assumed, in arriving at Eq. (4.9b) for $\tilde{E}_K[n]$, that the variation in the effective potential $V(r)$ can be neglected; it is to be expected that a more precise formulation of this condition is the requirement

$$\left| \frac{1}{V(r)} \frac{dV}{dr} \lambda\!\!\!^{-}(r) \right| \ll 1\ , \tag{9.1}$$

where $\lambda\!\!\!^{-}(r) = \lambda(r)/2\pi$ and $\lambda(r) \equiv h/p_F(r)$ defines a local wavelength. Over the bulk of the atom—normally this will refer to regions neither too near the origin nor too near the surface, but for the immediate consideration we need only exclude the surface region—$V(r)$ can be reasonably approximated by $\tilde{V}(r) \approx -(Ze^2/r)e^{-\alpha r}$ with α of the order of $Z^{1/3}/a_0$; using $p_F^2(r)/2m \approx -\tilde{V}(r)$, ignoring numerical factors of order unity, and, since we are concerned with the bulk of the electrons, choosing a characteristic value of r to be $a_0/Z^{1/3}$, we find that the condition becomes

$$Z^{-1/3} \ll 1\ .$$

If terribly far from a rigorous proof, the argument strongly suggests that TF theory becomes exact as $Z \sim \infty$. A formal proof was provided by Lieb and Simon (1973); see also Lieb and Simon (1977) and Lieb (1981) and references therein. Lieb and Simon partition coordinate space into boxes with dimensions which shrink as $Z^{-1/3}$ as $Z \sim \infty$, in each of which they are able to obtain upper and lower bounds on the energy which converge to order $Z^{7/3}$ to the TF energy estimate. (The upper and lower bounds are obtained by replacing the potential V in each box by its maximum and minimum values, respectively, and imposing Dirichlet and Neumann boundary conditions on the wave function at the walls of the box.)

The above discussion suggests that the fractional error for large Z might be of the order of $Z^{-1/3}$, which, for $Z=64$, is 25% (with the sign of the error undetermined). In fact, a comparison with experimental results shows the error to be somewhat less in magnitude. To put the discussion on a more quantitative basis we begin by seeking the correction of fractional order $Z^{-1/3}$, the Z^2 correction to E_{TF}.

B. The Scott Z^2 correction

The effective potential near the origin is $V(r) = -Ze^2/r$, and the condition (9.1) reduces to $(a_0/Zr)^{1/2} \ll 1$, which is obviously not satisfied for r very close to the origin. The net effect, as will be seen, is that there is a correction to E_{TF} which is proportional to Z^2, as first suggested some *25 years* after the work of Thomas and Fermi (Scott, 1952). It is clear that TF theory also treats the electrons near the surface incorrectly, since $V(r)$ in that region varies rapidly so that Eq. (9.1) is not satisfied. However, the energy per electron in that region is very small, so that even though there are a fair number of electrons near the surface, the energy contribution of the surface electrons can be expected to be negligible compared to the Z^2 dependence, which is our immediate concern.

The exact numerical coefficient of the Z^2 term has now been rigorously established, upper bounds (Siedentop and Weikard, 1987a, 1987b), and lower bounds (Hughes, 1986; Siedentop and Weikard, 1989) on the energy, to order Z^2, giving the same result. Important as it is, the proof is long and difficult, and we shall limit the discussion to qualitative but reasonably convincing arguments which, it so happens, give that same exact numerical coefficient.

1. An analysis based on a model Hamiltonian

The Coulomb interactions with one another of the inner electrons, in a region for which TF theory is not valid, will be negligible compared to their interactions with the nucleus. This suggests that we consider a model in which the e^-e^- interactions are neglected *throughout* the atom or ion. The Hamiltonian, to be denoted by $H^{(a)}$, is then a sum of hydrogenic Hamiltonians and the model problem is exactly solvable. For N electrons, the ground-state energy $E^{(a)}(N,Z)$ is that for which the lowest Q shells are filled, and a fraction ϕ of the shell with principal quantum number $Q+1$ is filled. [We are following the heuristic argument of Lieb (1976), slightly generalized to allow for an ion as well as a neutral atom.] We then have

$$\begin{aligned} E^{(a)}(N,Z)/\mathrm{Ry} &= \sum_{n=1}^{Q} 2n^2(-Z^2/n^2) \\ &\quad +2\phi(Q+1)^2[-Z^2/(Q+1)^2] \\ &= -2Z^2(Q+\phi)\ , \end{aligned} \tag{9.2}$$

where

$$\sum_{n=1}^{Q} 2n^2+2\phi(Q+1)^2=N\ , \tag{9.3}$$

or

$$Q^3=(3/2)N-3(\tfrac{1}{2}+\phi)Q^2+O(Q)\ . \tag{9.4}$$

For N greater than some very small value—we shall be more precise later in Sec. XI.C—we can solve Eq. (9.4) by iteration, to find

$$Q=(3N/2)^{1/3}-\tfrac{1}{2}-\phi+\cdots\ . \tag{9.5}$$

Equation (9.2) can then be written as

$$\begin{aligned} E^{(a)}(N,Z)/\mathrm{Ry} &= -2(3/2)^{1/3}Z^{7/3}(N/Z)^{1/3} \\ &\quad +Z^2+O(Z^{5/3})\ . \end{aligned} \tag{9.6}$$

The first term on the right-hand side of Eq. (9.6) appears in Eq. (5.25a) for E_{TF} (model ion)/Ry; we label that first term $E_{\mathrm{TF}}^{(a)}(N,Z)$. (Note that, as for a real atom, the TF ground-state energy of the model problem becomes exact as $Z\sim\infty$.) We therefore have

$$E^{(a)}(N,Z)-E_{\mathrm{TF}}^{(a)}(N,Z)=Z^2\mathrm{Ry}+\cdots\ .$$

(Since the difference originates in the effects of the inner electrons only, it is not surprising that the result is independent of N.) Now it is not unreasonable to assume that $E(N,Z)-E_{\mathrm{TF}}(N,Z)$ and $E^{(a)}(N,Z)-E_{\mathrm{TF}}^{(a)}(N,Z)$ have identical Z^2 coefficients, since the leading term of each difference comes from inner electrons, and there the true and model problems are presumably the same to leading order, since the e^-e^- interaction in the true problem can presumably be neglected in the inner region, as can the interaction of the outer with the inner electrons. We therefore expect—there is no question of proof here—that

$$E(N,Z)=E_{\mathrm{TF}}(N,Z)+Z^2\mathrm{Ry}+\cdots\ . \tag{9.7a}$$

This result applies to ions as well as atoms. However, there is no analytic form for $E_{\mathrm{TF}}(N,Z)$ for $N\neq Z$, but if we consider $N=Z$ and set $E(Z,Z)=E(Z)$ and $E_{\mathrm{TF}}(Z,Z)=E_{\mathrm{TF}}(Z)$, we have the analytic form

$$E(Z)=-c_7Z^{7/3}\mathrm{Ry}+Z^2\mathrm{Ry}+\cdots\ . \tag{9.7b}$$

2. A direct analysis of the inner electrons

The problem of the Z^2 correction for the neutral atom has also been considered by Schwinger (1980). He assumes that TF theory is inadequate for individual electron energies below $-\epsilon$, where

$$\frac{-Ze^2}{a_0/Z} \ll -\epsilon \ll -\frac{Ze^2}{a_0/Z^{1/3}}\ . \tag{9.8}$$

[If we express ϵ as Ze^2 over a length, Eq. (9.8) is equivalent to the assumption that TF theory is inadequate from the origin out to some value of r much larger than the K-shell radius a_0/Z and much smaller than the TF atomic radius $a_0/Z^{1/3}$.] The contribution $E_{\mathrm{TF\,in}}$ to E_{TF} from the strongly bound *inner* electrons, those with energies below $-\epsilon$, is therefore extracted and replaced by a more accurate estimate to be described shortly and to be denoted by $E_{\mathrm{better\ in}}$. The energy correction associated with the inner electrons is then

$$\Delta E_{\mathrm{in}}=-E_{\mathrm{TF\,in}}+E_{\mathrm{better\ in}}\ . \tag{9.9}$$

To evaluate $E_{\mathrm{TF\,in}}$, we use the virial theorem to set $-E_{\mathrm{TF}}=E_K$, and to write

$$-E_{\mathrm{TF\,in}}=+\int{}''2\frac{d\mathbf{r}\,d\mathbf{p}}{(2\pi\hbar)^3}\frac{p^2}{2m_e}\ , \tag{9.10a}$$

where the range of integration is defined by

$$0\le p(r)\le p_F(r),\quad p_F^2(r)/2m_e+V(r)=-\epsilon\ . \tag{9.10b}$$

The only electrons that can have an energy below the low-lying value $-\epsilon$ are those very close to the origin, and we can therefore approximate $V(R)$ in Eq. (9.10b) by

$$V_{\rm in}(r) \equiv -(Ze^2/r)+\epsilon_0 \ . \tag{9.11}$$

Here ϵ_0 is the energy of interaction of an inner electron with the potential generated at the origin by all of the electrons. Equation (9.11) follows from Eq. (5.8b), where, since we are here considering a neutral atom, we have set $\epsilon_F=0$, and where, using Eqs. (5.9a) and (5.9c),

$$\epsilon_0=(\tfrac{7}{3})c_7 Z^{4/3}{\rm Ry} \ . \tag{9.12}$$

(ϵ_0 can be derived differently, in a line. Equate

$$dE/dZ=-(\tfrac{7}{3})c_7 Z^{4/3}{\rm Ry}$$

obtained from the TF result for $E(z)$ with

$$dE/dZ=\sum_i(-e^2/r_i)=-\epsilon_0$$

obtained via the Hellmann-Feynman theorem.) From Eq. (9.10b), with V approximated by $V_{\rm in}$, and from the requirement that $p_F^2(r)\geq 0$, it follows that the range of interaction of r in Eq. (9.10a) is

$$0<r\leq Ze^2/\epsilon' \ , \tag{9.13}$$

where

$$\epsilon' \equiv \epsilon+\epsilon_0 \ . \tag{9.14}$$

[Using Eqs. (9.14) and (9.8), we find that Eq. (9.13) becomes $0\leq r\leq Ze^2/\epsilon \ll a_0/Z^{1/3}$, as expected.] The evaluation of $-E_{\rm TF\ in}$ is now straightforward. We find

$$\begin{aligned}-E_{\rm TF\ in}&=\frac{2}{5\pi}\frac{1}{\hbar^3 m_e}\int_0^{Ze^2/\epsilon'}\left[2m_e\left[\frac{Ze^2}{r}-\epsilon'\right]\right]^{5/2} r^2\,dr\\&=2Z^2{\rm Ry}(Z^2{\rm Ry}/\epsilon')^{1/2} \ .\end{aligned} \tag{9.15}$$

We turn now to the evaluation of $E_{\rm better\ in}$. Having used the virial theorem to work with E_K in the evaluation of $E_{\rm TF\ in}$, the energy to be extracted, we find it natural to do the same in obtaining a better estimate of the energies of the inner electrons. Since these electrons experience the potential $V_{\rm in}(r)$, and since kinetic energies are unaffected by a constant potential, the kinetic energy of the inner electrons, $E_{\rm K\ in}$, is that of electrons in a Coulomb field $-Ze^2/r$, and we have

$$\begin{aligned}E_{\rm better\ in}=-E_{K\ \rm in}&=-\sum_{n=1}^{Q_{\rm in}}(2n^2)(Z^2{\rm Ry}/n^2)\\&=-2Z^2Q_{\rm in}{\rm Ry} \ ,\end{aligned} \tag{9.16}$$

where $Q_{\rm in}$ is the maximum principal quantum number of the inner electrons. (We neglect the relatively few inner electrons in open shells, since these represent a correction on the correction $\Delta E_{\rm in}$.) The requirement that even the least energetic of the inner electrons have an energy below $-\epsilon$ is given by

$$-(Z^2/Q_{\rm in}^2){\rm Ry}+\epsilon_0\leq-\epsilon \ ,$$

which leads to

$$Q_{\rm in}=[(Z^2{\rm Ry}/\epsilon')^{1/2}] \ , \tag{9.17}$$

where, using a standard notation $[x]$ represents the largest integer less than or equal to x. We therefore have

$$E_{\rm better\ in}=-2Z^2{\rm Ry}[(Z^2{\rm Ry}/\epsilon')^{1/2}] \ . \tag{9.18}$$

With Eqs. (9.15) and (9.18), Eq. (9.9) becomes

$$\Delta E_{\rm in}=2Z^2(y-[y]){\rm Ry} \ ,$$

where

$$y\equiv Z^2{\rm Ry}/\epsilon' \ .$$

Independent of the precise value of y, and therefore of ϵ' and thus of ϵ, $y-[y]$ ranges linearly from 0 to 1 as y ranges from one integer to the next, so that to leading order $y-[y]$ is to be replaced by 1/2, and we have $\Delta E_{\rm in}=Z^2{\rm Ry}$, in agreement with our earlier result, Eq. (9.8). The fact that ϵ did not have to be specified other than through Eq. (9.8) adds greatly to the confidence one has in the result; Schwinger emphasizes "the seamless way in which the correct treatment of strongly bound electrons has been grafted onto the Thomas-Fermi model."

Now Eq. (9.8) can be rewritten as

$$Z^{-1/3}\left[\frac{Z^2{\rm Ry}}{\epsilon'}\right]^{1/2}\ll\left[\frac{\epsilon}{2\epsilon'}\right]^{1/2}\ll\left[\frac{Z^2{\rm Ry}}{\epsilon'}\right]^{1/2} \ . \tag{9.19}$$

But, by Eq. (9.12), ϵ_0 is of order $Z^{4/3}{\rm Ry}$, while by Eq. (9.8) $\epsilon\gg Z^{4/3}{\rm Ry}$, so that $\epsilon\gg\epsilon_0$ and $(\epsilon/2\epsilon')^{1/2}$ is of order unity. By Eqs. (9.17) and (9.19), we therefore have, noting that $t\gg 1$ implies $[t]\gg 1$,

$$1\ll Q_{\rm in}\ll Z^{1/3} \ . \tag{9.20}$$

Schwinger can therefore state "Any value of $Q_{\rm in}$ obeying Eq. (9.20) is acceptable, or, inasmuch as the basic parameter $Z^{1/3}$ is supposed to be very large, $Q_{\rm in}$ can be chosen to be any large Z-independent number." (The notation and numbering has been changed to that of the present article.)

With $Q_{\rm in}\gg 1$, we note for later reference that the number of inner electrons is

$$N_{\rm in}=\sum_{n=1}^{Q_{\rm in}}2n^2\approx\tfrac{2}{3}Q_{\rm in}^3\approx\tfrac{2}{3}(Z^2{\rm Ry}/\epsilon')^{3/2} \ . \tag{9.21a}$$

Using $Q_{\rm in}\ll Z^{1/3}$, by Eq. (9.20), we also have

$$N_{\rm in}\ll\tfrac{2}{3}Z \ . \tag{9.21b}$$

One must, of course, have $N_{\rm in}\ll Z$ if the present approach of concentrating on inner electron effects is to have any meaning.

Schwinger's use of the virial theorem in the above analysis shortens the calculation and warrants a further comment. Thus the virial theorem is valid for the entire system but not for the inner electrons alone. The net effect of the outer electrons on the (strongly bound) inner electrons is, however, of a higher order in Z, and that justifies the use of the virial theorem in the study of the inner electrons. A less clever though slightly more tedious approach, but one which is perhaps physically clearer, is to calculate the TF energy to be extracted by calculating the corrections to the individual terms whose sum defines the energy. The kinetic-energy correction is given by the right-hand side of Eq. (9.15), and its extraction gives

$$\Delta E_K = -2Z^2\mathrm{Ry}(Z^2\mathrm{Ry}/\epsilon')^{1/2} . \tag{9.22}$$

A very similar analysis gives for the extracted electron-nucleus interaction

$$\Delta E_{ev} = 4Z^2\mathrm{Ry}(Z^2\mathrm{Ry}/\epsilon')^{1/2} , \tag{9.23}$$

and, as is to be expected, one also finds that ΔE_{ee} is of a lower order in Z. $\Delta E_{\mathrm{TF\,in}} = \Delta E_K + \Delta E_{ev}$ is then again given by Eq. (9.15). The evaluation of $E_{\mathrm{better\,in}}$ now involves a sum of total energies rather than of kinetic energies. The only difference from the previous estimation, given in Eq. (9.18), is the effect of the outer electrons, through the generation of the potential approximated by ϵ_0, an effect expected to be negligible. Indeed, that difference is

$$\delta = N_{\mathrm{in}}\epsilon_0 ,$$

with N_{in} defined by Eq. (9.21a). Using Eq. (9.17), we see that δ *is* of lower order in Z than the term in Eq. (9.18), so that the use of the full E_{TF} gives the same result as that obtained by using the virial theorem. [It is interesting to observe, as can readily be checked by using Eq. (9.21), that, to within numerical constants of order unity, $|\Delta E_K|$ as defined by Eq. (9.22) is just the energy of N_{in} fermions of mass m_e confined to a sphere of radius Ze^2/ϵ', which, by Eq. (4.3), is

$$N_{\mathrm{in}}^{5/3}\hbar^2/[m_e(Ze^2/\epsilon')^2] ,$$

while ΔE_{ev} as given by Eq. (9.23) is just $N_{\mathrm{in}}Ze^2/(Ze^2/\epsilon')$.]

As a consistency check, note that the calculation of N_{in} via

$$N_{\mathrm{in}} = \int\int'' 2\frac{d\mathbf{r}\,d\mathbf{p}}{(2\pi\hbar)^3} ,$$

where the range of integration is defined by Eq. (9.10b), gives the same result, to leading order in Z, as that given by Eq. (9.21).

Working with N_{in}, Schwinger also makes contact with the original Scott (1952) calculation, and he also obtains some relativistic corrections to the TF theory.

The reader is urged to study the paper by Schwinger (1980). Even apart from the fact that the original papers often provide special insights, there is the additional material just referred to, and the pleasure to be derived from reading a paper written in Schwinger's style.

We turn now to the $Z^{5/3}$ correction.

X. A SECOND STEP BEYOND THOMAS-FERMI: THE EXCHANGE AND BULK-ELECTRON $Z^{5/3}$ CORRECTIONS

There are two separate $Z^{5/3}$ corrections. The origin of the first lies in exchange effects, while that of the second lies in the fact that even the bulk electrons, the very large fraction (for $Z \gg 1$) near neither the origin nor the surface, experience a slightly varying potential. (Schwinger refers to the $Z^{5/3}$ term as the second correction, and the Z^2 term discussed above as the first correction.)

A. The exchange correction

Hartree-Fock theory is often used as a starting point in the derivation of the exchange correction, but, following Schwinger (1981), we give a much simpler derivation which takes TF theory itself as the starting point.

Since there are no exchange corrections associated with one-particle operators, we need only consider the two-particle electron-electron interaction energy $\tilde{E}_{ee}[n]$ defined by Eq. (4.9d). n is given by

$$n(\mathbf{r}) = \int''[2d\mathbf{p}/(2\pi\hbar)^3]1 , \tag{10.1}$$

where the range of p is defined by Eq. (9.10b). (In this section we shall use m, rather than m_e, for the mass of the electron.) Equation (4.9d) contains $n(\mathbf{r})$ and $n(\mathbf{r}')$, and the upper limits $p_F(\mathbf{r})$ and $p_F(\mathbf{r}')$ are different. However, as will be seen very shortly, the momenta $\mathbf{p}$ and $\mathbf{p}'$ appear in the factors $\exp i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')/\hbar$ and $\exp i\mathbf{p}'\cdot(\mathbf{r}-\mathbf{r}')/\hbar$, respectively. For $\mathbf{r}$ very close to $\mathbf{r}'$ there is little difference between $p_F(\mathbf{r})$ and $p_F(\mathbf{r}')$; for $|\mathbf{r}-\mathbf{r}'| \gg \hbar/p_F$, with $\hbar/p_F$ having a characteristic value $a_0/Z^{2/3}$ which is much smaller than the characteristic TF radius $a_0/Z^{1/3}$, the contribution to the integral is negligible. [We used $p_F^2(\mathbf{r}) = -2mV(\mathbf{r})$, with $V(\mathbf{r}) \approx -Ze^2/(Z^{-1/3}a_0)$.] We can therefore replace both $p_F(\mathbf{r})$ and $p_F(\mathbf{r}')$ by, for example, $p_F(\mathbf{R})$, where $\mathbf{R} = (1/2)(\mathbf{r}_1+\mathbf{r}_2)$. We introduced a unit operator in Eq. (10.1), which we now choose to write as

$$1 = \phi_{\mathbf{p}}^*(\mathbf{r})\phi_{\mathbf{p}}(\mathbf{r}) ,$$

where

$$\phi_{\mathbf{p}}(\mathbf{r}) \equiv \exp(i\mathbf{p}\cdot\mathbf{r}/\hbar) .$$

We have thereby "made explicit the underlying wave functions." $\tilde{E}_{ee}[n]$ then contains products of two-particle wave functions,

$$[\phi_{\mathbf{p}}^*(\mathbf{r})\phi_{\mathbf{p}'}^*(\mathbf{r}')][\phi_{\mathbf{p}'}(\mathbf{r}')\phi_{\mathbf{p}}(\mathbf{r})] \equiv [\Psi_{\mathbf{p},\mathbf{p}'}^*(\mathbf{r},\mathbf{r}')]\Psi_{\mathbf{p},\mathbf{p}'}(\mathbf{r},\mathbf{r}')] . \tag{10.2}$$

The purpose of having introduced two factors of unity is to be in a position to implement exchange effects, for two electrons with the same spin projection must have a spatially antisymmetric wave function. For electrons with the same spin projection we therefore make the replacement

$$\Psi_{\mathbf{p},\mathbf{p}'}(\mathbf{r},\mathbf{r}') \to \{\Psi_{\mathbf{p},\mathbf{p}'}(\mathbf{r},\mathbf{r}') - \Psi_{\mathbf{p},\mathbf{p}'}(\mathbf{r}',\mathbf{r})\}/2^{1/2} ,$$

and we make a similar replacement for $\Psi^*_{\mathbf{p},\mathbf{p}'}(\mathbf{r},\mathbf{r}')$. This leads to the replacement of the product [ ][ ] of Eq. (10.2) by [ ][ ] $-\phi^*_{\mathbf{p}}(\mathbf{r})\phi^*_{\mathbf{p}'}(\mathbf{r}')\phi_{\mathbf{p}'}(\mathbf{r})\phi_{\mathbf{p}}(\mathbf{r}')$. $\widetilde{E}_{ee}[n]$ is thereby replaced by $\widetilde{E}_{ee}[n]+\widetilde{E}_{ex}[n]$; changing variables from $\mathbf{r}$ and $\mathbf{r}'$ to

$$\mathbf{R} \equiv \tfrac{1}{2}(\mathbf{r}+\mathbf{r}') \text{ and } \boldsymbol{\rho} \equiv \mathbf{r}-\mathbf{r}' ,$$

and noting that $\int d\mathbf{r} \int d\mathbf{r}' \cdots = \int d\mathbf{R} \int d\boldsymbol{\rho} \ldots$, gives the exchange contribution

$$\widetilde{E}_{ex}[n] = -\tfrac{1}{2}\times 2 \int d\mathbf{R} \int d\boldsymbol{\rho} |I(\boldsymbol{\rho})|^2 e^2/\rho , \qquad (10.3)$$

where there is only *one* spin factor of 2 since the spin projection of one electron determines that of the other for the spin case considered, and where

$$\begin{aligned} I(\boldsymbol{\rho}) &\equiv \int{}'' d\mathbf{p} \exp(-i\mathbf{p}\cdot\boldsymbol{\rho}/\hbar)/(2\pi\hbar)^3 \\ &= [1/(2\pi\hbar)^3] \int_0^{p_F(R)} 4\pi p^2 dp\, j_0(p\rho/\hbar) \\ &= [p_F^3(R)/2\pi^2\hbar^3](\sin y - \cos y)/y^3 , \quad y \equiv p_F(R)\rho/\hbar . \end{aligned}$$

We now use

$$\int_0^\infty y^2 dy (1/y)[(\sin y - y \cos y)/y^3]^2 = 1/4$$

to arrive at

$$\widetilde{E}_{\mathrm{ex}}[n] = -(e^2/4\pi^3) \int d\mathbf{r} [p_F(\mathbf{r})/\hbar]^4 , \qquad (10.4\text{a})$$

where we have changed the dummy variable $\mathbf{R}$ to $\mathbf{r}$. In terms of the number density $n(\mathbf{r})$, we have

$$\widetilde{E}_{ex}[n] = -(e^2/4\pi^3)(3\pi^2)^{4/3} \int n^{4/3}(\mathbf{r}) d\mathbf{r} . \qquad (10.4\text{b})$$

This result provides some justification for the addition of a term of the form of Eq. (10.4b) to the Lenz energy functional in Sec. V.B.2.a. A functional that includes such a term is referred to as the Thomas-Fermi-Dirac (or TFD) theory, but, even though the numerical coefficient in Eq. (10.4) is replaced by an arbitrary coefficient, TFD theory is somewhat flawed, since it accounts for the $Z^{5/3}$ energy correction but not the (larger) Scott Z^2 correction. [TFD theory is of considerable mathematical interest and does have some interesting physical features (Lieb, 1981)]. To obtain numerical results it is convenient to work with $V(r) = -(Ze^2/r)\phi(x)$ rather than with $n(r)$, for, by Eq. (4.16a), one then has $p_F^2(r) = 2mZe^2\phi(x)/r$. Using Eq. (5.4), Eq. (10.4a) then gives

$$E_{ex} = -(4/\pi^2)(3\pi/4)^{2/3} Z^{5/3} \mathrm{Ry} \int_0^\infty \phi^2(x) dx , \qquad (10.5)$$

and the numerical value of the integral is known to be 0.6154. The final result is therefore

$$E_{ex} = -0.4416 Z^{5/3} \mathrm{Ry} . \qquad (10.6)$$

B. The bulk electrons in a slowly varying potential

1. The effect on the entire atom

The assumption that the effective TF potential V_{TF} satisfies Eq. (9.1), that is, that the relative change in $V_{\mathrm{TF}}(r)$ can be neglected over the minimum distance, of order $\lambda\!\!\!^{-}(r)$, required to define the momentum well enough to have $\Delta p \ll p$, is reasonably well satisfied, but of course $V_{\mathrm{TF}}(r)$ does vary, and we shall now study the effects of that variation on the bulk of the electrons. The first effort to correct for the variation of the potential was made by von Weizsäcker (1935), but the result obtained was shown to be too large by a factor of 9 (Kirzhnits, 1957; Kompaneets and Pavlovskii, 1957; Hodges, 1973). Plindov and Dmitrieva (1978) obtained the presumably true $Z^{5/3}$ correction, but in doing so did not obtain the correct Z^2 correction. The first derivation to obtain what we believe to be the true Z^2 and $Z^{5/3}$ corrections is that of Schwinger (1981). Filling in a few steps and adding a few disimprovements, we follow his derivation.

We begin by finding a new expression for $n(\mathbf{r})$. Thus we note that, for a real number a,

$$(1/2\pi i) \int_C (dt/t) \exp(iat) = \Theta(a) ,$$

where the contour C runs from $-\infty$ to $+\infty$ along the real axis, passing below the origin, and where $\Theta(a)$ is the step function, defined by $\Theta(a)=1$ for $a \geq 0$ and $\Theta(a)=0$ for $a<0$. We then introduce the operator P, defined by

$$P = (1/2\pi i) \int_C (dt/t) \exp(-iHt/\hbar) , \qquad (10.7)$$

and observe that if $H\psi_l = E_l\psi_l$, then $P\psi_l = \Theta(-E_l/\hbar)$, that is, P is a projection operator that reproduces negative-energy (bound) states and annihilates positive-energy states. P is therefore the sum over all (normalized) bound-state wave functions,

$$P = \sum_{\mathrm{bd}} |\psi_{\mathrm{bd}}\rangle\langle\psi_{\mathrm{bd}}| ,$$

so that

$$\langle \mathbf{r}|P|\mathbf{r}\rangle = \sum_{\mathrm{bd}} |\psi_{\mathrm{bd}}(\mathbf{r})|^2 .$$

With a factor of 2 to account for spin, the electron number density, contributed to (by assumption) by all bound electrons, is given by

$$n(\mathbf{r}) = 2\langle \mathbf{r}|P|\mathbf{r}\rangle . \qquad (10.8\text{a})$$

We let

$$\langle \mathbf{r},t|\mathbf{r},0\rangle = \langle \mathbf{r}|e^{-iHt/\hbar}|\mathbf{r}\rangle \qquad (10.8\text{b})$$

be the time translation factor; for a system which is known to be at precisely the point $\mathbf{r}$ at the time $t=0$, $\langle \mathbf{r},t|\mathbf{r},0\rangle$ represents the probability amplitude that the system will be at precisely the same point at the later time t.

Equations (10.7) and (10.8) then give

$$n(\mathbf{r})=(1/\pi i)\int_C (dt/t)\langle \mathbf{r},t|\mathbf{r},0\rangle \ . \qquad (10.9)$$

Now (semiclassical) TF theory is a local theory, with any one of the functions $n(\mathbf{r})$, $p_F(\mathbf{r})$, and $V(\mathbf{r})$ expressible in terms of either of the other two at the same point $\mathbf{r}$. To go beyond TF theory, we must allow the value of, say, the effective potential V at $\mathbf{r}$, and in the neighborhood of $\mathbf{r}$, to determine $n(\mathbf{r})$ and $p_F(\mathbf{r})$. We do so by introducing a potential that is a reasonable approximation and that allows a relatively simple analysis, namely, a harmonic-oscillator-like potential. Thus we assume that by an appropriate choice of origin, of axes, and of the parameters v_0, $\boldsymbol{\omega}$, and $\mathbf{r}_1$ (with everything $\mathbf{r}_0$ dependent), the potential $V(\mathbf{r})$ in the neighborhood of $\mathbf{r}_0$, where $\mathbf{r}_0$ lies in the region occupied by the bulk electrons, can be adequately represented by

$$V(\mathbf{r})=v_x(x)+v_y(y)+v_z(z) \ , \qquad (10.10a)$$

where

$$v_x(x)=v_0+(m\omega_x^2/2)(x-x_1)^2 \ , \qquad (10.10b)$$

with $v_y(y)$ and $v_z(z)$ having similar forms. It follows from Eq. (10.10b) that

$$\omega_x^2=(1/m)d^2v_x(x)/dx^2 \qquad (10.11a)$$

and that

$$m\omega_x^4(x-x_1)^2=(1/m)[dv_x(x)/dx]^2 \ . \qquad (10.11b)$$

We cannot deduce from Eq. (10.11a) whether ω_x^2 for $\mathbf{r}$ in the neighborhood of $\mathbf{r}_0$ is positive or negative. (Note that ω_x itself never enters, for we shall be concerned with even functions of ω_x only; negative values of ω_x^2 therefore pose no problem.) It will be seen shortly [Eqs. (10.12) and (10.13a) below] that $\langle \mathbf{r},t|\mathbf{r},0\rangle$ contains an oscillatory time-dependent exponential, so that the integral in Eq. (10.9) converges; we can therefore introduce a convergence factor when, later, we make approximations that cause that integral to diverge.

It follows from Eq. (10.10a) that the motions along the x, y, and z axes are independent. We therefore have

$$\langle \mathbf{r},t|\mathbf{r},0\rangle=\langle x,t|x,0\rangle\langle y,t|y,0\rangle\langle z,t|z,0\rangle \ , \qquad (10.12)$$

with the factors known since the potentials are harmonic-oscillator-like; see, for example, Finkelstein (1973). We have

$$\langle x,t|x,0\rangle=\left[\frac{m\omega_x}{2\pi i\hbar\sin\omega_x t}\right]^{1/2}\exp[-(i/\hbar)v_0t]\exp[-(i/\hbar)m\omega_x(x-x_1)^2\tan(\omega_x t/2)] \ . \qquad (10.13a)$$

Since $v_x(x)$ is assumed to be slowly varying, it follows from Eq. (10.11a) that ω_x^2 is small, and we expand about $\omega_x=0$. Retaining for the moment only the leading term in $\sin\omega_x t$ and in $\tan(\omega_x t/2)$ gives

$$\langle x,t|x,0\rangle\approx\left[\frac{m}{2\pi i\hbar t}\right]^{1/2}\exp\left[-\frac{iv_x(x)t}{\hbar}\right]=\langle x,t|x,0\rangle_{\mathrm{TF}} \ , \qquad (10.13b)$$

where $v_x(x)$ is given by Eq. (10.10a). The identification in Eq. (10.13b) of the approximate form of $\langle x,t|x,0\rangle$ with the TF time transformation function $\langle x,t|x,0\rangle_{\mathrm{TF}}$ can be justified as follows. With that identification, Eq. (10.12) is approximated by

$$\langle \mathbf{r},t|\mathbf{r},0\rangle_{\mathrm{TF}}=\left[\frac{m}{2\pi i\hbar t}\right]^{3/2}\exp\left[-\frac{itV(\mathbf{r})}{\hbar}\right] \ , \qquad (10.14a)$$

and the use of this expression in the TF version of Eq. (10.9),

$$n_{\mathrm{TF}}(\mathbf{r})=(1/\pi i)\int_C (dt/t)\langle \mathbf{r},t|\mathbf{r},0\rangle_{\mathrm{TF}} \ ,$$

gives

$$n_{\mathrm{TF}}(\mathbf{r})=\frac{1}{\pi r}\left[\frac{m}{2\pi i\hbar}\right]^{3/2}\int_C\frac{dt}{t^{5/2}}\exp\left[-\frac{itV(\mathbf{r})}{\hbar}\right] \ .$$

Setting $u=-tV(\mathbf{r})/\hbar$ and using

$$\int_C u^{-5/2}e^{iu}du=-(8/3)\pi^{1/2}e^{i\pi/4} \ ,$$

we find

$$n_{\mathrm{TF}}(\mathbf{r})=(1/3\pi^2)[-2mV(\mathbf{r})/\hbar^2]^{3/2}$$
$$=(1/3\pi^2)[p_F(\mathbf{r})/\hbar]^3 \ , \qquad (10.14b)$$

in agreement with Eq. (4.11).

Rather than validating the expression for $\langle x,t|x,0\rangle_{\mathrm{TF}}$ given by Eq. (10.13b) by showing that it leads to an $n_{\mathrm{TF}}(\mathbf{r})$ which agrees with the number density of TF theory, we can validate that expression itself. We begin by noting that the $\langle x,t|x,0\rangle_{\mathrm{TF}}$ of Eq. (10.13b) can be rewritten as

$$\langle x,t|x,0\rangle_{\mathrm{TF}}$$
$$=\int_{-\infty}^{\infty}\frac{dp_x}{2\pi\hbar}\exp\left[-\frac{it}{\hbar}\left[\frac{p_x^2}{2m}+v_x(x)\right]\right] \ . \qquad (10.15)$$

But now consider the one-dimensional version of Eq. (10.8b), under the assumption that the momentum and coordinate operators commute, that is, under the assumption that corrections of order $\hbar$ can be neglected, consistent with TF theory in which $\hbar$ enters only in determining the number of states allowed in a given region of phase space. The insertion of the unit operator

$$\int_{-\infty}^{\infty}|p_x\rangle dp_x\langle p_x|$$

between the exponential and $|x\rangle$ in the one-dimensional version of Eq. (10.8b) then gives Eq. (10.15). (Some related material will be discussed in Sec. XI.D.)

To go beyond TF, we retain one further term in the expansions of $\sin\omega_x t$ and of $\tan(\omega_x t/2)$ in Eq. (10.13), with a convergence factor understood. We write

$$(\omega_x/\sin\omega_x t)^{1/2}\approx t^{-1/2}[1+(\omega_x^2t^2/12)]$$

and

$$\exp(-ib\omega_x^4t^3)\approx 1-ib\omega_x^4t^3\,,$$

$$b\equiv m(x-x_1)^2/(24\hbar)\,,$$

and arrive at

$$\langle x,t|x,0\rangle\approx\langle x,t|x,0\rangle_{\mathrm{TF}}\left[1+\frac{\omega_x^2t^2}{12}-\frac{im\omega_x^4(x-x_1)^2t^3}{24\hbar}\right].$$

Using Eq. (10.11), this becomes

$$\langle x,t|x,0\rangle\approx\langle x,t|x,0\rangle_{\mathrm{TF}}\left[1+\frac{1}{m}\left[\frac{d^2v_x}{dx^2}\right]\frac{t^2}{12}-\frac{i}{m}\left[\frac{dv_x}{dx}\right]^2\frac{t^3}{24\hbar}\right].$$

We can replace $v_x(x)$ by $V(\mathbf{r})$, and then, again neglecting higher-order terms, we arrive at

$$\langle \mathbf{r},t|\mathbf{r},0\rangle\approx\langle \mathbf{r},t|\mathbf{r},0\rangle_{\mathrm{TF}}\left[1+(\nabla^2V)\frac{t^2}{12m}-i(\nabla V)^2\frac{t^3}{24m\hbar}\right].$$

On substituting this expression into Eq. (10.9), we find that the unit term on the right leads, as noted earlier, to $n_{\mathrm{TF}}(\mathbf{r})$, and, replacing t^j with $j=2$ or 3 by $(i\hbar d/dV)^j$, we obtain

$$\begin{aligned}n(\mathbf{r})-n_{\mathrm{TF}}(\mathbf{r})&=-\frac{\hbar^2}{12m}\nabla^2V\frac{d^2}{dV^2}n_{\mathrm{TF}}-\frac{\hbar^2}{24m}(\nabla V)^2\frac{d^3}{dV^3}n_{\mathrm{TF}}\\&=-\frac{m}{12\pi^2\hbar}\frac{\nabla^2V}{(-2mV)^{1/2}}-\frac{m^2}{24\pi^2\hbar}\frac{(\nabla V)^2}{(-2mV)^{3/2}}=\delta n(\mathbf{r})\,.\end{aligned}\qquad(10.16)$$

Since, in the region of the bulk electrons, $V(\mathbf{r})$ will be close to $V_{\mathrm{TF}}(\mathbf{r})$, and since $n_{\mathrm{TF}}(\mathbf{r})$ and $V_{\mathrm{TF}}(\mathbf{r})$ are known, we have an explicit expression for $\delta n(\mathbf{r})$ on replacing $V(\mathbf{r})$ by $V_{\mathrm{TF}}(\mathbf{r})$ in Eq. (10.16). This explicit correction for the number density may well be a more useful result than the $Z^{5/3}$ energy correction term which we are about to obtain. Note that δn is of order $(-mV_{\mathrm{TF}}/\hbar^2)^{1/2}/l^2$, or $(Z/a_0)^{1/2}/l^{5/2}$, where l is a characteristic distance of a bulk electron from the nucleus, which can be taken to be $a_0/Z^{1/3}$. δn is therefore of the order of $Z^{4/3}/a_0^3$. Since n is of the order of $Z/(a_0/Z^{1/3})^3=Z^2/a_0^3$, we have

$$\delta n/n=O(Z^{-2/3})\,.\qquad(10.17)$$

To obtain the change in the energy generated by the change δn in n given by Eq. (10.16), we *cannot* simply replace n_{TF} in the Lenz energy functional of Eq. (4.9) by $n=n_{\mathrm{TF}}+\delta n$; since the functional is stationary with respect to variations in n about n_{TF}, the correction will be of relative order $(\delta n/n)^2$, that is, by Eq. (10.17), of relative order $Z^{-4/3}$, and therefore of absolute order $Z^{7/3}\times Z^{-4/3}$, or Z. To obtain the $Z^{5/3}$ correction term, we must change the Lenz energy functional $\tilde{E}[n]$ in a more significant manner; we must add a term to $\tilde{E}[n]$ such that the variation of the new functional leads *not* to Eq. (10.14b), satisfied by $n=n_{\mathrm{TF}}$ and $V=V_{\mathrm{TF}}$, but to Eq. (10.16). We can rewrite Eq. (10.16), to the relevant order, as

$$(5k\hbar^2/3m)n^{2/3}(\mathbf{r})=-V(\mathbf{r})+S(\mathbf{r})\,,\qquad(10.18)$$

where we used Eq. (4.9g) and where

$$S\equiv\frac{\hbar^2}{24m}\left[\frac{\nabla^2V}{V}-\frac{1}{4}\frac{(\nabla V)^2}{V^2}\right].\qquad(10.19)$$

Schwinger expresses the additional term in the functional required to generate $S(\mathbf{r})$ in terms of $n(\mathbf{r})$, since the Lenz energy functional is normally expressed in terms of $n(\mathbf{r})$, and then reexpresses the additional term in terms of V. We are interested in the energy correction rather than the corrected functional, and we can proceed directly (with some loss of insight). Thus we seek a functional $g[V]$ such that

$$\begin{aligned}\delta g[V]&=-\int S(r)\delta n(r)d\mathbf{r}\\&=-\int S(r)\frac{dn}{dV}\delta V\,d\mathbf{r}\,,\end{aligned}\qquad(10.20)$$

$g[V]$ will then represent the additional energy. It is sufficient to use Eq. (10.14b) for the evaluation of dn/dV; this gives

$$\frac{dn}{dV}=-\frac{3}{2}\left[\frac{3m}{5k\hbar^2}\right]^{3/2}(-V)^{1/2}\,. \qquad (10.20')$$

Choosing

$$g[V]=\frac{1}{96\pi^2 m\hbar}\int d\mathbf{r}(-2mV)^{3/2}\left[\frac{\nabla V}{V}\right]^2\,, \qquad (10.21)$$

one finds that $\delta g[V]$ differs from the desired expression, defined by Eqs. (10.20), (10.19), and (10.20′), by a term proportional to

$$\mathcal{L}\equiv\int\nabla\cdot\mathbf{J}\,d\mathbf{r},\quad \mathbf{J}\equiv\delta V(\nabla V)/(-V)^{1/2}\,.$$

When $\mathcal{L}$ is converted to a surface integral the contribution from the surface at $r\sim\infty$ vanishes. In obtaining the contribution from the surface at $r\sim 0$ we can use the fact that

$$V(r)\sim-(Ze^2/r)+\epsilon_0^*\equiv V_{\rm in}^*(r),\quad r\sim 0\,, \qquad (10.22)$$

where ϵ_0^* is a constant whose value need not concern us. [It will be close to ϵ_0, given by Eq. (9.12).] We then find that

$$\mathcal{L}=4\pi r^2\delta V(r)\frac{dV_{\rm in}^*(r)}{dr}\frac{1}{[-V_{\rm in}^*(r)]^{1/2}}\Bigg|^{r=0}$$
$$=4\pi Ze^2 r^{1/2}\delta V(r)|^{r=0}\,.$$

Since we know that $V(r)$ for ~ 0 must have the form given by Eq. (10.22), it follows that $\delta V(r)\sim$const for $r\sim 0$, and therefore that $\mathcal{L}=0$, and finally that Eq. (10.21) would seem to be the desired functional.

2. The extraction of the inner-electron effects

We are not yet home. In fact, since $V(r)$ has a $1/r$ singularity at the origin, the integral in Eq. (10.21) for $g[V]$ diverges. The source of the difficulty is quite clear. Recall that, in obtaining the "first correction" to TF theory, we deleted the contribution given by TF theory for electrons with energies below $-\epsilon$, where bounds on ϵ are given by Eq. (9.8). This was done because electrons with energies below $-\epsilon$ lie in the inner region, where the condition (9.1), an assumption basic to the validity of TF theory, is far from satisfied. We then added on the energy of inner electrons interacting Coulombically with the nucleus, with an additional energy ϵ_0, given by Eq. (9.12), for each inner electron by virtue of the interaction of each inner electron with all of the outer electrons. But the treatment presented above for the bulk electrons also treats electrons with energies below $-\epsilon$ incorrectly. We must therefore delete the contribution of those electrons from Eq. (10.21). We shall *not*, however, add anything; to the required accuracy, that is, through terms of order $Z^{5/3}$, the corrected energy contribution of the inner electrons has been obtained, the correction being given by Eq. (9.7).

To perform the deletion from $g[V]$, we begin by using the identity

$$(-V)^{3/2}(\nabla V/V)^2=-2(\nabla V)\cdot\nabla(-V)^{1/2}$$
$$=2(-V)^{1/2}\nabla^2V+(4/3)\nabla^2(-V)^{3/2}\,.$$

Equation (10.21) then becomes

$$g[V]=(24\pi^2\hbar)^{-1}\{g_1[V]+g_2[V]\}\,, \qquad (10.23a)$$

where

$$g_1[V]\equiv\int d\mathbf{r}(-2mV)^{1/2}\nabla^2V\,, \qquad (10.23b)$$

$$g_2[V]\equiv(3m)^{-1}\int d\mathbf{r}\nabla^2(-2mV)^{3/2}\,. \qquad (10.23c)$$

We then observe that for electrons with energies below $-\epsilon$ the upper limit on $p_F(\mathbf{r})$ is not $[-2mV(\mathbf{r})]^{1/2}$, as for electrons required only to have energies below zero, but $[-2m(V+\epsilon)]^{1/2}$; furthermore, since strongly bound electrons are present only for small r, we can replace V in $-(V+\epsilon)$ by $V_{\rm in}^*$, given by Eq. (10.22). [It would make little difference if, throughout this discussion, we were to use $V_{\rm in}$, defined by Eq. (9.11), rather than $V_{\rm in}^*$.] Thus the energy to be deleted is obtained by using Eq. (10.23), with $-V$ replaced by $-V_{\rm in}^*-\epsilon$; note, though, that whereas r ranges from 0 to ∞ in Eq. (10.23), in the term to be extracted r ranges only from 0 to $r_\epsilon'^*=Ze^2/\epsilon'^*$ (where $\epsilon'^*=\epsilon_0^*+\epsilon$), the value of r at which $(-V_{\rm in}^*-\epsilon)^{1/2}$ ceases to be real.

We first consider $g_2[V]+g_2[V_{\rm in}^*+\epsilon]$. Converting to surface terms, the $g_2[V]$ term vanishes at $r=\infty$ while the $g_2[V_{\rm in}^*+\epsilon]$ term vanishes at $r=r_{\epsilon'}^*$, and we remain with the difference

$$(-3m)^{-1}(2m)^{1/2}4\pi r^2\frac{d}{dr}[(-V_{\rm in}^*)^{3/2}$$
$$-(-V_{\rm in}^*-\epsilon)^{3/2}]|^{r=0}\,,$$

where we used $-V\sim-V_{\rm in}^*$ as $r\sim 0$. Using Eq. (10.22), we find that this difference vanishes.

We turn now to $g_1[V]-g_1[V_{\rm in}^*+\epsilon]$. Since

$$(-V)^{1/2}\nabla^2V=(-V)^{1/2}4\pi e^2[Z\delta(\mathbf{r})-n(\mathbf{r})]$$

and

$$(-V)^{1/2}\delta(\mathbf{r})=(-V_{\rm in}^*)^{1/2}\delta(\mathbf{r})$$

while

$$(-V_{\rm in}^*)^{1/2}\nabla^2V_{\rm in}^*=4\pi Ze^2(-V_{\rm in}^*)^{1/2}\delta(\mathbf{r})\,,$$

the difference of the g_1's is $-4\pi n(\mathbf{r})e^2(-2mV)^{1/2}$, and, deleting the inner-electron contribution from $g[V]$ of Eq. (10.23a), the first quantum correction of the kinetic energy is

$$E_{\rm qu}=(24\pi^2\hbar)^{-1}\{(g_1[V]+g_1[V_{\rm in}^*+\epsilon])+(g_2[V]$$
$$+g_2[V_{\rm in}^*+\epsilon])\}$$
$$=(24\pi^2\hbar)^{-1}\int(-2mV)^{1/2}(-4\pi e^2n)d\mathbf{r}\,. \qquad (10.24)$$

The small difference between n and $n_{\rm TF}$ can here be ignored. Using $(-2mV)^{1/2}=p_F$ and Eq. (4.11), and comparing the result with Eq. (10.4a), we obtain

$$E_{\rm qu}=(2/9)E_{\rm ex} \ . \tag{10.24$'$}$$

(The use of the subscript qu does not, of course, imply that other corrections are not quantum in origin.) The total $Z^{5/3}$ correction is then, using Eq. (10.6).

$$E_{\rm qu}+E_{\rm ex}=(11/9)E_{\rm ex}=-0.5398Z^{5/3}{\rm Ry} \ . \tag{10.25}$$

The reader, urged at the end of Sec. IX to study Schwinger's 1980 paper, is urged even more strongly to study Schwinger's 1981 paper.

XI. NOTES

A. A numerical study of $E(Z)$ for large-Z atoms

The results obtained in Eqs. (5.9c), (9.7b), and (10.25) give, for the energy of a neutral atom,

$$E(Z)=(-c_7Z^{7/3}-c_6Z^2-c_5Z^{5/3}){\rm Ry}+\ldots \ , \tag{11.1}$$

where

$$c_7=1.537\,490\,24\ldots, \quad c_6=-1, \quad c_5=0.5398 \ . \tag{11.2}$$

The values of c_7 and c_6 have been rigorously established, and whatever small doubt there may be as to the result for c_5 can be reduced even further by a numerical study. To minimize the effect of corrections beyond $Z^{5/3}$, be they lower powers of Z or trigonometric functions of Z, one considers $E(Z)$ for Z as large as one can readily perform the (*nonrelativistic*) calculations. This was done for a few values of Z ranging up to $Z=290$. It was *assumed* that the correction was of the form $-c_4Z^{4/3}$Ry, and, since the analysis was performed before the value of c_6 had been firmly established, a few different values of c_6, including $c_6=-1$, were considered (Shakeshaft, Spruch, and Mann, 1981). From the results of that analysis for $c_6=-1$, c_5 is found to be 0.55, with an error of order ± 0.02, quite close to the expected value, given in Eq. (11.2), and c_4 is found to be quite close to zero.

B. Improved estimate of the ratio of $|E_{ev}(Z)|$ to $E_{ee}(Z)$

Given the Z^2 and $Z^{5/3}$ corrections, it is trivial (Chen and Spruch, 1987) to obtain a better estimate of the ratio of $|E_{ev}(Z)|$ to $E_{ee}(Z)$ than its TF value of 7. One uses the virial theorem in the form $E_{ev}(Z)+E_{ee}(Z)=2E(Z)$, one shows that in the TF approximation

$$E_{ev}(Z)\approx Z\,dE(Z)/dZ$$

is in error by at most of order $Z^{4/3}$, and, using Eq. (11.1), one thereby arrives at

$$\frac{|E_{ev}(Z)|}{E_{ee}(Z)}\approx\frac{\sum nc_nZ^{(n-7)/3}}{\sum(n-6)c_nZ^{(n-7)/3}} \ ,$$

where each sum is over $n=7$, 6, and 5. Apart from its intrinsic interest, the improved ratio can provide a useful check on nonrelativistic energy calculations, and it is also useful in the analysis of very low-energy β-decay processes (less than, or of the order of 10 keV for large Z), for which the difference in the atomic binding energies of the parent and daughter nuclei is important, or even crucial.

As one example, consider the β decay of ^{187}Re into ^{187}Os, a decay of great interest in studies of the age of our galaxy (Clayton, 1983). On energetic grounds, by an amount $\Delta\approx 3$ keV, an isolated ^{187}Re *nucleus* cannot decay; the difference in atomic binding energies of Re and Os atoms (with $Z=75$ and 76, respectively), of the order of 15 keV, more than compensates for Δ and allows a Re *atom* to decay. (See, for example, Chen, Rosenberg, and Spruch, 1987, and references therein.)

C. The surprising accuracy of TF theory for rather small values of Z

In the model in which the electron-electron interaction is neglected, one arrives at Eq. (9.4), and one then obtains Q (the largest principal quantum number for which the shell is full) in terms of the number N of electrons as a power series in $N^{-1/3}$. It has been shown (Shakeshaft and Spruch, 1981) that such an expansion converges for

$$N>1/(18\sqrt{3}) \ , \tag{11.3}$$

a *very* small number, and converges rapidly for $N>1$. [For simplicity, consider only neutral atoms by setting $N=Z$. For fixed Z, the value of Q defined by Eq. (9.3) is a discontinuous function of Z, and this leads to B Eq. (9.2); these discontinuities persist in models that include screening effects to some extent *and* in the solvable model in which all pairs of particles interact via harmonic-oscillator potentials. The discontinuities strongly suggest that the energy cannot be expanded to all orders in a power series in $Z^{-1/3}$.] Since $|E_{ev}|/E_{ee}$ is of the order of seven, even the unscreened model is of some merit, and, with $N=Z$, the domain of validity defined by Eq. (11.3) makes it plausible that even though TF theory is often thought of as being useful only for $Z\gg 1$, it in fact gives meaningful results even for Z rather small. As Schwinger (1980) points out, it even works reasonably well for hydrogen, for which the application of a statistical theory makes no sense. [Keeping only the c_7 term gives $E(Z=1)=-1.53\ldots$Ry, off by about 50%. Keeping the c_7,c_6, and c_5 terms in Eq. (11.1) gives the ridiculously good answer $E(Z=1)=-1.08$Ry.]

D. Improvements upon TF theory: a slightly different derivation and two applications

Semiclassical TF theory has been used by many authors to estimate a wide range of entities. These include various sums over normalized hydrogenlike eigenfunctions, $\phi_{\nu\lambda\mu}(\mathbf{r})$—see, for example, Sec. VII of Shakeshaft and Spruch (1979)—sums that arise in a number of physical problems. The question arises to what extent improvements upon TF theory, such as those discussed in Secs. IX and X, can be used to improve the different TF estimates.

We consider, in particular,

$$n_\nu(r) \equiv 2\sum_{\lambda,\mu} |\phi_{\nu\lambda\mu}(\mathbf{r})|^2 ,$$

the number density of electrons filling the νth shell, where the electrons interact with the nucleus (of charge Z) but not with one another. In the TF approximation we have

$$n_{\nu,\mathrm{TF}}(r) = \int 2\, d\mathbf{p}/(2\pi\hbar)^3 ,$$

where the range of p is defined by

$$E_{\nu-1} \le (p^2/2m) - (Ze^2/r) \le E_\nu ,$$

with $E_\nu = -(Z^2/\nu^2)\mathrm{Ry}$. For $\nu \gg 1$, we find

$$n_{\nu,\mathrm{TF}}(r) = \frac{2^{1/2}Z^2 m^{1/2}}{\pi^2 \nu^3 \hbar a_0^2}\left[E_\nu + \frac{Ze^2}{r}\right]^{1/2} .$$

This result is not valid for $r \approx 0$, but of greater present interest is that the result breaks down at the classical radius, $r_{\mathrm{class}} = 2\nu^2 a_0/Z$, the value of r at which $E_\nu = Ze^2/r$ (and the maximum value of r for the given ν in the Bohr model, which occurs for $\lambda = 0$).

We now seek to improve upon the TF estimate of $n_\nu(r)$. The approach to be used is that of Shakeshaft and Spruch (1981). It differs from that of Schwinger (1981) and Englert and Schwinger (1984) only in some minor mathematical details and reproduces a number of their results. Let $n(r,E)$ be the number density for electrons filling all shells with energy below E. For $\nu \gg 1$ we then have

$$n_\nu(r) \approx n(r,E_\nu) - n(r,E_{\nu-1})$$
$$\approx \frac{\partial n(r,E)}{\partial E}\bigg|^{E=E_\nu} \left[\frac{2Z^2}{n^3}\mathrm{Ry}\right] ,$$

the last factor being an approximation to $E_{\nu-1} - E_\nu$. We have

$$n(r,E) = 2\langle \mathbf{r}|P_E|\mathbf{r}\rangle ,$$

where, following Schwinger, with

$$-i(H-E)t/\hbar = [-ip^2t/2m\hbar] + [-i(V-E)t/\hbar]$$
$$\equiv A + B ,$$

we have

$$P_E = (1/2\pi i)\int_C (dt/t)\exp(A+B) .$$

[In lowest approximation, we assume that A and B commute. We then have

$$e^{A+B}|\mathbf{r}\rangle \cong \int e^B e^A |\mathbf{p}\rangle d\mathbf{p}\langle \mathbf{p}|\mathbf{r}\rangle ,$$

with $|\mathbf{p}\rangle$ an appropriately normalized plane wave, and the operator p^2 in A can be replaced by the number p^2. One then finds that $n(r,E)$ reduces to the TF result.] Assuming that third- and higher-order derivatives of $V(r)$ are negligible in the region of r that makes a significant contribution to $n_\nu(r)$, we need only retain second-order commutators in the Campbell-Baker-Hausdorff expansion of $\exp(A+B)$, as given, for example, by Hausner and Schwartz (1968). The neglect of terms with three or more derivatives in all, such as $(\nabla^2 V)\nabla V$, and some further (reasonable) approximations on terms that are small then reproduces some of the Schwinger (1981) and Englert-Schwinger (1984, 1985) results. [This is hardly surprising since the omission of third- and higher-order derivatives of $V(\mathbf{r})$ is equivalent to the use of a harmonic-oscillator potential.] As applied to $n_\nu(r)$, for $\nu = 10$ and $Z = 1$, the improved result extends the region where the approximation is meaningful from $r_{\mathrm{class}}/a_0 = 200$ to roughly $r/a_0 \approx 230$. [In obtaining the result, an integral was evaluated numerically. It had not been realized that the integral had been evaluated analytically, in terms of an Airy function and its derivative, by Englert and Schwinger (1984).] The fractional extension may not seem to be impressive, but the result may be very significant nevertheless, since many atomic properties are determined by the outer electrons. It should be stressed that the example chosen is a much harsher test of the Schwinger and Englert-Schwinger modifications of TF theory than a study of a neutral atom would be, since the effective $V(r)$ experienced by ν-shell electrons is much more variable than the V that would be experienced by the electrons in a real neutral atom.

The improved TF form has also been used to estimate the diamagnetic susceptibility χ of the inert gases. This too is a harsh test of the formalism, for since χ is approximately equal to $\sum_i r_i^2$—its form in the independent-particle model—it depends strongly on the surface properties of the atoms. Although the results (De Raad and Schwinger, 1982) were "considerably better than those of Thomas-Fermi, the predictions are still significantly in excess of the experimental values."

E. Shell structure

Even the very patient reader may wonder when, if ever, the question of shell structure, so basic to atomic theory, will be discussed. In fact, the discontinuities noted in subsection X.B above are not at arbitrary values of N but at values representing closed shells. However, the energy corrections associated with these discontinuities are rather small; important as it is, shell structure plays only a minor role in the determination of $E(Z)$, and the proof—or even an indication—of its existence in a study from first principles of $E(Z)$ is difficult. Very considerable progress along these lines has been made by Englert and Schwinger (1985).

We here restrict ourselves to a few simple remarks. We note that in the unscreened model (in which the electron-electron interaction is ignored) the coefficient c_5 of the $Z^{5/3}$ term is not constant; rather, it is the sum of a constant term and a term that varies sinusoidally with Z. However, for a model that includes screening to some extent, such as the model in which an electron with a given principal quantum number is shielded by all electrons with smaller principal quantum numbers, c_5 is a constant (Shakeshaft and Spruch, 1981). The existence of shell structure suggests that an expansion of $E(Z)$ as a power series in $Z^{-1/3}$ breaks down at some point; it need not suggest that that breakdown cannot be obtained from a statistical model.

F. The potential value of improved TF theories

As noted earlier, TF theory and its extensions have an enormous advantage over the Schrödinger theory which they approximate in that TF theory is expressed in terms of a function of one variable, $n(\mathbf{r})$, rather than a function of Γ variables, $\Psi=\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_\Gamma)$, where Γ is the number of electrons and nuclei in the system. (That is of course also true of density-functional theory, but the TF approach is perhaps more basic.) That $n(\mathbf{r})$ satisfies a nonlinear equation, as opposed to the linear (Schrödinger) equation satisfied by Ψ, is a relatively minor disadvantage. TF theory does have a number of very serious disadvantages. It is neither sufficiently accurate nor sufficiently wide-ranging for most present atomic purposes. (The ground-state energy estimates are meaningful but inaccurate, and useful wave functions are not generated. Furthermore, it is not applicable to excited states. In addition, the TF treatment of the outer electrons, often the most important electrons in the study of the interaction of an atom with an external electric or magnetic field and of the scattering of an electron or another atom, is very poor.) Then, too, TF theory is not applicable at all to molecules. An improved TF theory that generated an $n(\mathbf{r})$ accurate for all regions of the atom and that was applicable and accurate for a molecule could be *extremely* useful, even if the equation that defined $n(\mathbf{r})$ was quite complicated, since the complexity of the determination of the many-variable Ψ increases much more rapidly as the, say, molecule becomes more complex than would the determination of $n(\mathbf{r})$, and analysis of $n(\mathbf{r})$ would surely be simpler than that of Ψ for a sufficiently heavy molecule. The work initiated by Schwinger (1980, 1981), and continued in a series of papers which can be traced back from Englert and Schwinger (1985), seems very promising in this regard. It would be amusing if, more than half a century after Thomas and Fermi introduced their theory, further improvements of that theory could lead to a formulation that, for a wide and important class of problems, was more useful than Schrödinger theory.

Notes added in proof

(1) For a short interesting paper which includes a discussion of some recent developments, see Thirring, W. E., 1990, Found. Phys. **20**, 1103.

(2) The value of the coefficient c_5 of $Z^{5/3}$ cited in Sec. X has now been shown to be exact; see Fefferman, C. L. and Seco, L. A., 1990, Bull. Amer. Math. Soc. **84**, 1239.

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APPENDIX A: PROOF THAT $\tilde{E}[n_t]\geq\tilde{E}[n]$

Our Lenz energy functional is defined by Eq. (4.9). The condition $\delta\tilde{E}[n]\geq 0$ led to an $n(\mathbf{r})$ defined by Eq. (4.20). We showed in Sec. IV.B.2 that $\tilde{E}[n_t]\geq\tilde{E}[n]$ for $n_t(\mathbf{r})=n(\mathbf{r})+\delta n(\mathbf{r})$ normalized and $\delta n(\mathbf{r})$ small but otherwise arbitrary. We now wish to generalize this to show that $\tilde{E}[n_t]\geq\tilde{E}[n]$ for $n_t(\mathbf{r})=n(\mathbf{r})+\Delta n(\mathbf{r})$ normalized, where $\Delta n(\mathbf{r})$ need *not* be small. The proof is of the same form for a neutral atom and for a positive ion. We have

$$\tilde{E}[n_t]=\tilde{E}[n]+\int \Delta n(\mathbf{r})\left\{-\frac{Ze^2}{r}+2\frac{e^2}{2}\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\right\}d\mathbf{r}+k(\hbar^2/m_e)\int[n_t^{5/3}(\mathbf{r})-n^{5/3}(\mathbf{r})]d\mathbf{r}+S[\Delta n]\ ,$$

where $S[x]$ is given by the equations above Eq. (4.21a), so that $S[\Delta n]\geq 0$. By Eqs. (4.13a) and (4.13b), the curly bracket in the expression for $\tilde{E}[n_t]$ satisfies

$$\{\ \}\geq -(5/3)k(\hbar^2/m_e)n^{2/3}(\mathbf{r})-\mu \ .$$

We therefore have

$$\tilde{E}[n_t]-\tilde{E}[n]\geq k(\hbar^2/m_e)\int \{n_t^{5/3}+(2/3)n^{5/3}-(5/3)n^{2/3}n_t\}d\mathbf{r} \ ;$$

we used the fact that $-\mu\int(n_t-n)d\mathbf{r}=0$ since n_t and n have the same normalization. With $f(x)=n^{2/3}(\mathbf{r}),g(x)=n_t(\mathbf{r}),p=5/2$, and $q=5/3$, the Höder inequality given below Eq. (3.9) leads to

$$\int n^{2/3}n_t d\mathbf{r}\leq T^{2/5}T_t^{3/5}=Ty^{3/5} \ ,$$

where

$$T\equiv\int n^{5/3}d\mathbf{r}(>0) \ ,$$

$$T_t\equiv\int n_t^{5/3}d\mathbf{r}(>0) \ , \quad y\equiv T_t/T>0 \ .$$

We now have

$$\tilde{E}[n_t]-\tilde{E}[n]\geq(k\hbar^2/m_e)\{y+(2/3)-(5/3)y^{3/5}\}T\geq 0 \ ;$$

the curley bracket is non-negative for all (positive) y. It follows that $\tilde{E}[n_t]$ has its minimum at $n_t=n$.

APPENDIX B: THE "ESCAPE-VELOCITY EQUATION" AND THE VIRIAL THEOREM

One of the basic equations of Thomas-Fermi theory for a neutral atom is

$$p_F^2(r)/2m_e+V(r)=0 \ .$$

An (obviously incorrect) interpretation of this equation as implying that E_K+E_V is equal to zero would imply a violation of the virial theorem. The point, clearly, is that the virial theorem relates averages over all $\mathbf{r}$ of energies, while $p_F^2(r)/2m_e$ represents the maximum of the kinetic energy, and at a particular value of r. It is simple enough to check that the escape-velocity equation and the virial theorem are consistent with one another. The paradox can be resolved readily. To begin with, we note that the momentum distribution at point r is proportional to p^2dp for $p\leq p_F(r)$ and is equal to zero for $p>p_F(r)$. It follows that the average value of p^2 for the electrons at point r is given by

$$\langle p^2(r)\rangle=\int_0^{p_F(r)}p^2p^2dp\bigg/\int_0^{p_F(r)}p^2dp=(3/5)p_F^2(r) \ .$$

Second, we decompose the effective potential $V(r)$ into

$$V(r)=-(Ze^2/r)+V_{ee}(r) \ ,$$

thereby defining the contribution within the TF approximation of the electron-electron interaction $V_{ee}(r)$ to the effective potential $V(r)$ seen by an individual electron. See Eq. (4.15). At this stage we have

$$(5/3)\langle p^2(r)\rangle/2m_e-(Ze^2/r)+V_{ee}(r)=0 \ .$$

We multiply by the TF number density $n(r)$, integrate over $d\mathbf{r}$, and use

$$\int[\langle p^2(r)\rangle/2m_e]n(r)d\mathbf{r}=E_K \ ,$$

$$-Ze^2\int[n(r)/r]d\mathbf{r}=E_{ev} \ ,$$

and

$$\tfrac{1}{2}\int V_{ee}(r)n(r)d\mathbf{r}=E_{ee} \ .$$

The factor $\frac{1}{2}$ in the last relation is to avoid double counting. We now have

$$(5/3)E_K+E_{ev}+2E_{ee}=0 \ .$$

Since $E_{ev}=-7E_{ee}$ in TF theory—see Eq. (5.13)—we can write

$$E_{ev}+2E_{ee}=(5/6)(E_{ev}+E_{ee})=(5/6)E_V$$

and we have the virial theorem result, $2E_K+E_V=0$.

APPENDIX C: A LOWER BOUND ON THE KINETIC ENERGY OF A SYSTEM OF ELECTRONS AND OF FIXED NUCLEI

A sketch of the approach to be used

The determination of a lower bound on an energy level is normally difficult. The problem of obtaining a lower bound on $\tilde{E}_K[\psi]$, defined by Eq. (8.4b), is made even more difficult by the requirement, for present purposes, that the bound be a multiple of $\tilde{E}_K[n]$, defined by Eq. (4.9b). The truly difficult part is not the mathematics; it is to know how to proceed. A bound was first obtained by Lieb and Thirring (1975)—see also Lieb (1976)—who utilized upper and lower bounds on the ground-state energy $\mathcal{E}_{\mathrm{gd}}(\mathcal{H})$ of an appropriately chosen many-body Hamiltonian $\mathcal{H}$—*not* the Hamiltonian of physical interest.

With t_i the kinetic-energy operator of the ith electron, and with $\mathcal{V}$ an as yet unspecified many-body potential, we set

$$\mathcal{H}=\sum_{i=1}^{N_e}t_i+\mathcal{V} \ .$$

The Rayleigh-Ritz theorem then gives

$$\mathcal{E}_{\mathrm{gd}}(\mathcal{H}) \le \tilde{E}_K[\psi] + \langle \psi | \mathcal{V} | \psi \rangle .$$

If we can find a lower bound $\mathcal{E}_{\mathrm{gd,low}}(\mathcal{H})$ on $\mathcal{E}_{\mathrm{gd}}(\mathcal{H})$, we shall have a (formal) lower bound on the quantity of interest,

$$\tilde{E}_K[\psi] \ge \mathcal{E}_{\mathrm{gd,low}}(\mathcal{H}) - \langle \psi | \mathcal{V} | \psi \rangle . \tag{C1}$$

We then have to express the right-hand side as a multiple of $\tilde{E}_K[n]$.

The number of eigenvalues below *E* for a one-body problem

For reasons that will become clear later, we consider a *single* electron in a potential $V(\mathbf{r})$, as yet unspecified, and let $N_E(V)$ be the number of bound states with an energy below the energy E, where $E \le 0$. Assume for the moment that $V(\mathbf{r}) \le 0$ for all $\mathbf{r}$. Let $\psi_b(\mathbf{r})$ be a normalized bound-state wave function with energy E, for the potential $\lambda_b V(\mathbf{r})$. With $G(\mathbf{r},\mathbf{r}';E)$ defined by

$$(t-E)G(\mathbf{r},\mathbf{r}';E) = -\delta(\mathbf{r}-\mathbf{r}') ,$$

we have

$$G\lambda_b V \psi_b = \psi_b .$$

We set $-V(\mathbf{r}) = v^2(\mathbf{r})$, and $\phi_b = v\psi_b$, and arrive at

$$(-vGv)\phi_b = (1/\lambda_b)\phi_b . \tag{C2}$$

(The energy E is not an eigenvalue; it is fixed. The eigenvalues $1/\lambda_b$ of the Hermitian operator $-vGv$ determine the different potential strengths $\lambda_b V$ which give bound states of energy E). It follows that

$$\mathrm{Tr}(-vGv) = \mathrm{Tr}(GV) = \sum_b (1/\lambda_b) ,$$

but the result is useless since $G(\mathbf{r},\mathbf{r};E)$ is infinite, as is therefore the trace. However, Eq. (C2) implies

$$(vGv)^2 \phi_b = (1/\lambda_b^2)\phi_b ,$$

and it follows, since G is symmetric in $\mathbf{r}$ and $\mathbf{r}'$, that

$$\sum_b (1/\lambda_b^2) = \mathrm{Tr}(vGv)^2 = \mathrm{Tr}(GVGV) .$$

$$= \int\int d\mathbf{r}\, d\mathbf{r}'\, V(\mathbf{r}) G^2(\mathbf{r},\mathbf{r}';E) V(\mathbf{r}') \equiv I . \tag{C3}$$

Each $\lambda_b \le 1$ represents a bound state supported by $V(\mathbf{r})$ (see Fig. 2), and therefore

$$N_E(V) \le I .$$

G^2 is given by

$$G^2(\mathbf{r},\mathbf{r}';E) = \left[\frac{2m_e}{\hbar^2}\right]^2 \left[\frac{1}{4\pi}\right]^2 \frac{e^{-2K|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|^2} ,$$

where $E = -K^2\hbar^2/2m_e$. Introducing the Fourier transform

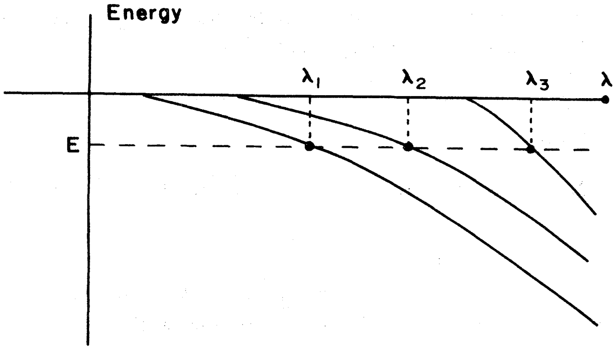

FIG. 2. Consider the potential $\lambda V(\mathbf{r})$. As one increases λ from zero, bound states appear at zero energy and move down monotonically. The eigenvalues λ_b are the values of λ for which there is a bound state at energy E. The bound states supported by V are those with $\lambda_b \le 1$. The schematic diagram is for the case of three bound states.

$$e^{-2K\rho}/\rho^2 = (1/2\pi)^3 \int a(\mathbf{k}) e^{i\mathbf{k}\cdot\boldsymbol{\rho}} d\mathbf{k} ,$$

one readily finds

$$a(\mathbf{k}) = 4\pi \int e^{-2K\rho}[(\sin k\rho)/k\rho] d\rho .$$

We can therefore rewrite I, defined by Eq. (C3), as

$$I = (4\pi)^{-2}(2m_e/\hbar^2)^2(2\pi)^{-3} J ,$$

where

$$J \equiv \int\int\int d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{k}\, V(\mathbf{r}) V(\mathbf{r}') a(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}$$

$$= \int d\mathbf{k}\, a(\mathbf{k}) \left| \int V(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \right|^2 .$$

Since $\sin x/x \le 1$, we have

$$a(k) \le a(0) = 4\pi/2K ,$$

and we obtain an upper bound on J by replacing $a(\mathbf{k})$ by $a(0)$. Rewriting the $|\ |^2$ in J as an integral over $\mathbf{r}$ and $\mathbf{r}'$, and integrating over $\mathbf{k}$, we find

$$J \le (2\pi)^3 a(0) \int d\mathbf{r}\, V^2(\mathbf{r}) ,$$

and therefore

$$N_E(V) \le I \le Q \int d\mathbf{r}\, V^2(\mathbf{r})/|E|^{1/2} , \tag{C4a}$$

where

$$Q \equiv (4\pi)^{-1}\tfrac{1}{2}(2m_e/\hbar^2)^{3/2} . \tag{C4b}$$

This result, in the slightly more general form discussed in the next paragraph, was obtained by Schwinger (1961) and Birman (1961). [Note that, since $G^2(\mathbf{r},\mathbf{r}';E) = G^2(\mathbf{r}-\mathbf{r}';E)$, I, as defined by Eq. (C3), is a convolution integral and can be bounded more readily by using Young's inequality.]

If $V(\mathbf{r})$ is not everywhere attractive, we replace it by its attractive component, $-|V(\mathbf{r})|_-$; we employ the notation $|f(\mathbf{r})|_- = -|f(\mathbf{r})|$ if $f(\mathbf{r}) \le 0$ and $|f(\mathbf{r})|_- = 0$ if $f(\mathbf{r}) > 0$. Since $V(\mathbf{r}) \ge -|V(\mathbf{r})|_-$, it follows that $N_E(V) \le N_E(-|V(\mathbf{r})|_-)$, and therefore that the inequality (C4) remains valid for $V(\mathbf{r})$ not everywhere attractive if $V^2(\mathbf{r})$ in the integral is replaced by $(|V(\mathbf{r})|_-)^2$. [Note that $E(\lambda)$, the energy of a particular energy level (continuous in λ) associated with $H(\lambda)=T+\lambda V$, is monotonic in λ even if $V(\mathbf{r})$ is not everywhere attractive. A proof can be based on the use of the eigenfunction ψ_λ associated with $E(\lambda)$ as a trial function in a Rayleigh-Ritz upper-bound determination of $E(\lambda+d\lambda)$.]

It will be convenient to consider not $N_E(V)$ but $N_{E/2}(-|V-\frac{1}{2}E|_-)$, and to observe that

$$N_E(V) \le N_{E/2}(-|V-\tfrac{1}{2}E|_-) \; . \qquad \text{(C5)}$$

[The difference between $h_- \equiv t - |V-\frac{1}{2}E|_-$ and $h \equiv t+V$ is

$$\begin{aligned} h_- - h &= \tfrac{1}{2}|E| \quad \text{where } V(\mathbf{r}) \le \tfrac{1}{2}E \; , \\ &= -V(\mathbf{r}) \quad \text{where } V(\mathbf{r}) > \tfrac{1}{2}E \; , \end{aligned}$$

that is, $h_- - h \le \frac{1}{2}|E|$. For each eigenvalue of h below E, there will therefore be an eigenvalue of h_- below $E+\frac{1}{2}|E| = -\frac{1}{2}E$. h_- could have additional eigenvalues below $\frac{1}{2}E$.]

The sum of the energy eigenvalues for a one-body problem

For V fixed there is an energy eigenvalue e_b associated with each strength parameter eigenvalue $\lambda_b \le 1$. $N_E(V)$ as a function of E is a staircase function (with unequal horizontal lengths), rising abruptly by one unit as it passes through an eigenvalue, ranging from 0 at $E=-\infty$ to B at $E=0$, where $B=N_0(V)$ is the number of bound states. We therefore have

$$\begin{aligned} \int_{-\infty}^{0} N_E(V)dE &= \int_{e_1}^{e_2} dE + \cdots + \int_{e_B}^{0} B\, dE \\ &= (e_2-e_1)+2(e_3-e_2)+\cdots+B(-e_b) \\ &= \sum_{b=1}^{B} |e_b| \; . \end{aligned}$$

[A geometrical proof of this result follows immediately from inspection of a plot of $N_E(V)$ versus E; the area under the curve is a sum of horizontal rectangles of unit height and of width $|e_b|$.)] Using Eqs. (C5) and (C4), we arrive at

$$\begin{aligned} \sum_b |e_b| &\le \int_{-\infty}^{0} N_{E/2}(-|V(\mathbf{r})-\tfrac{1}{2}E|_-)dE \\ &\le Q\int d\mathbf{r}\int_{-\infty}^{0}(-|V(\mathbf{r})-\tfrac{1}{2}E|_-)^2(2/|E|)^{1/2}dE \\ &= 2^{1/2}Q\int d\mathbf{r}\int_{2V}^{0}(V-\tfrac{1}{2}E)^2|E|^{-1/2}dE \\ &= (4/15\pi)(2m_e/\hbar^2)^{3/2}\int[-V(\mathbf{r})]^{5/2}d\mathbf{r} \; . \qquad \text{(C6)} \end{aligned}$$

[Had we directly used the bound on $N_E(V)$ to bound $\sum_b |e_b|$, rather than proceeding through the use of Eq. (C5), the bound would be proportional to $\int_{-\infty}^{0} dE/|E|^{1/2} = \infty$. We could cut off the lower limit at e_1 and obtain a finite result, but the result obtained would not be in a useful form.]

The sought-for bound

We are now in a position to choose a $\mathcal{V}$ for which a lower bound on $\mathcal{E}_{\rm gd}(\mathcal{H})$ can be found. Thus, having obtained a lower bound on $\sum e_b$ for the one-particle potential V, we choose $\mathcal{V}$ to be a sum of V's, that is,

$$\mathcal{H} = \sum_{i=1}^{N_e} [t_i + V(r_i)] \; .$$

For this independent-particle Hamiltonian, the lowest energy can surely be no lower than that obtained by placing two electrons (with opposite spin projections) in each state—and then only if $N_e \ge 2B$. We therefore have

$$\mathcal{E}_{\rm gd}(\mathcal{H}) \ge 2\sum_b e_b \; . \qquad \text{(C7)}$$

With Eq. (C1), we then have

$$\tilde{E}_K[\psi] \ge 2\textstyle\sum_b e_b - \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r} \; , \qquad \text{(C8)}$$

where we exploited the fact that $\mathcal{V}$ is a sum of one-particle operators. Inspecting Eq. (C6) and recalling that the right-hand side of Eq. (C8) is to be proportional to $\tilde{E}_K[n]$, we choose

$$(2m_e/\hbar^2)^{3/2}[-V(\mathbf{r})]^{5/2} = \beta(\hbar^2/2m_e)n^{5/3}(\mathbf{r}) \; ,$$

with β a dimensionless constant. Each of the two terms in Eq. (C8) is then indeed a multiple of $\tilde{E}_K[n]$, and, with the choice of β that gives the best lower bound, which is readily found to be $\beta=(3\pi/4)^{5/3}$, we have

$$\tilde{E}_K[\psi] \ge (4\pi)^{-2/3}\tilde{E}_K[n] \; . \qquad \text{(C9)}$$

We have at long last obtained the bound cited in Sec. VIII, but the question remains as to the quality of the result, that is, the extent to which one might be able to improve the bound by increasing the value of the coefficient. We gave a qualitative physical argument in Sec. VIII that the coefficient should be at most unity, and we now give a proof of that result, based on a concrete example; recall that the inequality (8.7) is to be valid for an arbitrary Hamiltonian and for ψ normalized and antisymmetrized but otherwise arbitrary. Thus consider the ground-state kinetic energy $E_K[\psi_{\rm ex}]$ of a large number N_e of noninteracting electrons in a cube L on a side, and ignore corrections of order $1/N_e$. Imposing periodic boundary conditions, we find that the *exact* wave function $\psi_{\rm ex}$ is an antisymmetrized product of plane waves of wave vectors $(2\pi/L)\boldsymbol{l}$, where the components of $\boldsymbol{l}$ are positive or negative integers or zero. We have

$$E_K[\psi_{\rm ex}]=(\hbar^2/2m_e)(2\pi/L)^2\sum_l l^2 ,$$

and we then find, for $N_e \gg 1$,

$$E_K[\psi_{\rm ex}]\approx k(\hbar^2/m_e)L^3 n_{\rm ex}^{5/3} ,$$

where k is defined by Eq. (4.9g) and $n_{\rm ex}=N_e/L^3$ is the exact constant number density, so that $E_K[\psi_{\rm ex}]=E_K[n_{\rm ex}]$.

It has been surmised that one might be able to raise the coefficient $(4\pi)^{-2/3}$ in Eq. (C9) to unity. This is perhaps suggested by an examination of the semiclassical value of $\sum_b e_b$, which, for $V(\mathbf{r})\le 0$, is given by

$$\left[\sum_b e_b\right]_{\rm semiclass}=\int\int\frac{d\mathbf{r}\,d\mathbf{p}}{(2\pi\hbar)^3}\left\{\frac{p^2}{2m_e}+V(\mathbf{r})\right\} ,$$

where the range of integration is defined by $\{\ \}\le 0$. One readily finds that the result is $1/4\pi$ times the bound on the quantum value of $\sum e_b$, given by Eq. (C6). This translates into the factor $(4\pi)^{-2/3}$ in calculating the bound on $\tilde{E}_K[\psi]$.

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