The above equations of the hierarchy are coupled with those of the electromagnetic field

$$(1/c^2)\ddot{\mathbf{A}}(\mathbf{r}) - \nabla^2\mathbf{A}(\mathbf{r}) = \frac{4\pi}{c}\mathbf{J}_T(\mathbf{r})\,, \quad (\text{IV.13})$$

where

$$\mathbf{J}_T(\mathbf{r}) = \mathbf{J}(\mathbf{r}) + \frac{1}{4\pi e^2}\int \frac{\partial}{\partial \mathbf{r}'}\, V(\mathbf{r}-\mathbf{r}')\cdot\frac{\partial}{\partial \mathbf{r}'}\,\mathbf{J}(\mathbf{r}')d\mathbf{r}'\,, \quad (\text{IV.14})$$

and

$$\mathbf{J}(\mathbf{r}) = \frac{e}{m}\int\left(\mathbf{p} - \frac{e}{c}\,\mathbf{A}(\mathbf{r})\right)\hat{f}_1(\mathbf{r},\mathbf{p})d\mathbf{p}\,. \quad (\text{IV.15})$$

The above equations constitute an alternate formulation of quantum electrodynamics in which bilinear products of the particle field operators have been eliminated in favor of phase space distribution functions. The field equations have the form of a generalized magnetohydrodynamics and indeed may be used as the starting point for the investigation of transport phenomena in quantum fluids.

The expectation values formed from these equations no longer satisfy closed sets of equations. In addition to the Wigner distribution $\langle\hat{f}\rangle$ and the average field $\langle\mathbf{A}(\mathbf{r})\rangle$, there arise Green's functions of the types $\langle\mathbf{A}(\mathbf{r})\mathbf{A}(\mathbf{r}')\rangle$, $\langle\hat{f}(\mathrm{x})\hat{f}(\mathrm{x}')\rangle$, and $\langle\hat{f}(\mathrm{x})\mathbf{A}(\mathbf{r}')\rangle$. Theories of irreversibility may be constructed if one makes various statistical assumptions concerning the structure of these Green's functions.

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On the Stability of Molecules in the Thomas-Fermi Theory

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THE Thomas-Fermi model has been used in approximating the properties of molecules.[1] On the other hand, Sheldon[2] finds no stable equilibrium in a calculation applying the Thomas-Fermi-Dirac model to the N_2 molecule. At the end of his paper, Sheldon gives arguments to support the view that similar calculations will not give rise to stable molecular binding. In the following a proof is given that statistical models cannot give rise to lower energies in the molecular state than obtained for the separated atoms. The proof applies to the stability of both neutral molecules and under certain conditions to positive molecular ions.

Consider first a fixed positive-charge distribution in space and an equal amount of negative charges carried by an electron gas which obeys the Thomas-Fermi equation

$$\Delta\varphi = \varphi^{3/2} - \rho_+\,. \quad (1)$$

Here $-e\varphi$ is the potential energy of the electrons measured in appropriate units which have been so adjusted as to eliminate numerical coefficients in the Thomas-Fermi equation. The term ρ_+ represents the positive charge density measured in appropriate units. This positive charge density is zero except within the spatial extension of the nuclei of the molecule in question. These locations are fixed and have been chosen without regard to the stability of the configuration. The proof is simpler if we do not consider the nuclei as point charges and do not introduce any singularities. This, of course, happens to correspond to physical reality. For the time being we shall consider neutral molecules. The potential φ and the quantity $\varphi^{3/2}$ are positive, and since ρ_+ is restricted to a finite region in space, φ approaches zero at great distances as $1/r^4$. This behavior is the same as for neutral atoms and is due to the fact that for $1/r^4$ both sides of (1) approach zero with the same power, namely, $1/r^6$.

Let us now add to the positive-charge distribution an infinitesimal additional positive charge near one location. This additional charge distribution shall be designated by ζ. Let us also introduce a corresponding electron distribution so as to keep the system strictly neutral. Then we can prove the following

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[1] A summary can be found in the seventh chapter of the book by P. Gombás, *Die Statistische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Berlin, 1949). Also S. Flügge, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. 36, p. 108.

[2] J. W. Sheldon, Phys. Rev. **99**, 1291 (1955).

lemma: The addition to the positive function φ is everywhere positive definite.

The new Thomas-Fermi equation is

$$\Delta(\varphi + \epsilon) = (\varphi + \epsilon)^{3/2} - (\rho_+ + \zeta) . \quad (2)$$

Considering that the function ϵ is infinitesimal one obtains from (2) and (1) the linear differential equation

$$\Delta\epsilon = \tfrac{3}{2}\,\varphi^{1/2}\epsilon - \zeta . \quad (3)$$

The value of ϵ cannot be negative at all locations because near the point where ζ has been introduced the effect of the positive charge surely predominates and the value of φ must increase. Let us now assume that ϵ has different signs in different regions of space. Then there will exist a region V not containing the additional charge ζ, inside of which ϵ has the opposite sign from the one that ϵ assumes near ζ. On the surface S of V, ϵ shall vanish.

In V the function ϵ satisfies the homogeneous linear differential equation

$$\Delta\epsilon = \tfrac{3}{2}\,\varphi^{1/2}\epsilon . \quad (4)$$

Considering that $\varphi^{1/2}$ is everywhere positive $\Delta\epsilon$ must be negative throughout V. But the gradient of ϵ cannot point inward along S, because $\epsilon = 0$ on S and $\epsilon < 0$ inside S. Therefore, the assumption that ϵ has different signs in different regions is disproved.

The statement remains correct if V extends in some directions to infinity. As we approach infinity ϵ approaches zero more rapidly than $1/r^4$ and thus the integration over S is not influenced by portions of S which lie at infinity.

We can furthermore see that ϵ cannot become zero in a volume, on a surface, a line, or a point. In fact, if that were the case and if ϵ is positive in the neighborhood of this region, surface, line, or point, we must again consider a bounding surface surrounding the region where $\epsilon = 0$ and close enough to that region. If we now let the bounding surface contract onto the region where $\epsilon = 0$, the volume integral of $\frac{3}{2}\,\varphi^{1/2}\,\epsilon$ always approaches zero more rapidly than the surface integral of $\nabla\epsilon$ since the former contains two more powers of the infinitesimal thickness of the region of integration in which $\epsilon \neq 0$. In case $\zeta \neq 0$, within the region the contradiction is even more sharp, since now the volume integral is carried out over $\frac{3}{2}\,\varphi^{1/2}\,\epsilon - \zeta$.

Thus, we can conclude that an increase of the charge ζ at any place will produce an increase of the potential φ at every place, which is the content of the lemma.

If we now compare an atom in which the nucleus has a charge equal to Z with a molecule in which the same nucleus occurs, it follows that at any selected distance from Z in the molecule φ is greater than φ at this same distance in the atom. Indeed, the molecule can be obtained from the atom by adding successively infinitesimal charges at the locations of the other nuclei and by adding each time the corresponding electronic-charge distribution. In this process φ steadily increases and so the resultant molecular φ function must be greater.

We are now prepared to prove that a neutral molecule in the Thomas-Fermi approximation always has a higher energy than the isolated atoms of which it consists. We shall start from a single atom. Next we shall compare two processes. In the first we shall begin to build up a second atom at a great distance. We shall do this by adding an infinitesimal positive charge at a time and follow this by adding enough electrons—distributed according to the Thomas-Fermi equation—to neutralize the positive charge. This is the atom-building process. The second process is carried out similarly, only the positive charges are added—in infinitesimal amounts—at a location near the first nucleus so that in the end a molecular solution should result. This is the molecule-building process.

In each of the two cases we shall consider the energy needed to carry out the addition of the charges. Of course, for the building up of a nucleus of small volume, a very great amount of positive energy is needed. But we have considered the positive charge as spread out and so no divergence will be encountered. Comparing the atom-building process to the molecule-building process we see that in building up the two nuclei in a similar fashion more energy is needed in each step of adding the positive charge in the molecule-building process. In fact, we have seen that, at corresponding locations measured from the nucleus being built, φ is higher in the molecule than in the corresponding location in the atom. Furthermore, φ is attractive for electrons; thus, it is repulsive for positive charges.

On the other hand, the additions of infinitesimal electron distributions, which alternate with the addition of the positive charges, do not change the energy. In a neutral system the electrons are filled up to the zero level. After each addition of an infinitesimal ζ an energy gain per electron proportional to ζ becomes available. But only an infinitesimal amount ζ is added to the negative charge. Thus, the energy is changed by a quantity proportional to ζ^2 and in the limiting case of $\zeta \to 0$ no contribution is made to the energy by these steps.

We see, therefore, that more energy is expended in the molecule-building process than in the atom-building process. After a diatomic molecule is completed a third nucleus is started—at an isolated location in one case, within the molecule in the other. The same arguments apply as above. In this way one can prove that the energy of any collection of isolated atoms is lower than any grouping of these atoms into a molecule.

The result which we have proved is, of course, by no means surprising. Indeed the formation of a stable molecule in the Thomas-Fermi model would lead to a rather peculiar situation. In this model a similarity transformation holds. If all nuclear charges are multiplied by a factor F then a new solution is obtained in which all distances are multiplied by $F^{-1/3}$ and all energies by $F^{7/3}$. Thus, if a molecule in the Thomas-Fermi model should turn out to be stable then another molecule, built of atoms with greater Z values, would have smaller equilibrium distances and a considerably higher binding energy.

The result obtained for the Thomas-Fermi approximation continues to hold if an exchange term is introduced and the Thomas-Fermi-Dirac approximation is used. In this case φ obeys the equation

$$\Delta\varphi = (\varphi^{1/2} + \kappa)^3 - \rho_+ . \tag{5}$$

At the surface of a neutral atom or molecule the potential φ vanishes and thus assumes the same value as at infinity. But at such a surface (at which, of course, ρ_+ is assumed to be zero) the term κ^3 persists and thus the electronic-charge density retains a finite value at the surface. Beyond the surface the charge density becomes abruptly zero. In this way the Thomas-Fermi-Dirac solutions for neutral structures are confined to finite volumes and do not extend to infinity.

If we now again introduce an infinitesimal localized positive perturbation to the charge density ρ_+ we obtain for the additional potential ϵ the equation

$$\Delta\epsilon = \frac{3}{2}\,\frac{(\varphi^{1/2} + \kappa)^2}{\varphi^{1/2}}\,\epsilon - \zeta . \tag{6}$$

This is an equation similar to our Eq. (3) and similar conclusions can be drawn as have been derived earlier for the Thomas-Fermi case. Specifically, it can be stated that a positive addition ζ inside the original electron cloud will cause an increase in φ at every location. However, this statement holds only for the finite volume inside which the original φ distribution was different from zero. All other noncontiguous regions representing other neutral atoms or molecules remain undisturbed.

The surface at which $\varphi = 0$ merits special attention. At the surface $\Delta\epsilon$ becomes singular. This indeed had to be expected. The perturbation extends the region in which the charge density, given by $\Delta\varphi$, has a value $\Delta\varphi \geqslant \kappa^3$. Thus, near the surface an infinitesimal change, ζ, produces a finite change in $\Delta\varphi$. This change extends only over an infinitesimal volume. While a finite change in $\Delta\varphi$ results the change in the potential, φ remains infinitesimal even on the surface.

As in the earlier proof of our lemma, no negative region can occur for ϵ that lies entirely inside the region where $\Delta\varphi > \kappa^3$. If the region of negative ϵ has a border coincident with the original surface where $\Delta\varphi = \kappa^3$ there results an infinitesimal strip in which the introduction of ζ reduces φ to the value zero. In this strip, Eq. (6) is not valid, and on the border of the strip, Eq. (6) gives a divergent result since the denominator $\varphi^{1/2}$ becomes zero.

But in spite of these complications, the function ϵ still is the difference between the new and old values of φ and thus Maxwell's equations must still hold for ϵ. On the border of the region in which ϵ is negative the gradients of ϵ point outward and nevertheless $\Delta\epsilon$ (i.e., the difference of $\Delta\varphi$ after the change and before it) is negative. These two statements are incompatible and so a region of negative ϵ values cannot be assumed.

A region, surface, line, or point where $\epsilon = 0$ inside, or extending into the volume where $\Delta\varphi > \kappa^3$, can likewise be ruled out. A portion of such a structure could be surrounded by a surface inside the volume where $\Delta\varphi > \kappa^3$ even though this surface may cut the region where $\epsilon = 0$. One can thus use the same argument as in the Thomas-Fermi case. Thus, we find $\epsilon > 0$ in every neutral atom or molecule to which the infinitesimal localized positive charge ζ and the corresponding electron distribution have been added.

The further steps of our argument follow in the same manner as for the Thomas-Fermi model. One can show in the same way as above that comparing corresponding locations in an atom and a molecule, made up of that atom and other atoms, φ is always greater for the molecule. One can further proceed to show that adding positive charges in the molecule-building process requires more work than in the corresponding steps during the atom-building process. Finally, the addition of electron distributions which alternate with the addition of positive charges, produces no additional energy terms. This last conclusion can be drawn because the increments ϵ of the potential remain infinitesimal in each step at all places—even on the surface of the Thomas-Fermi-Dirac distribution.

Thus, we have shown that no neutral molecule is stable in the Thomas-Fermi-Dirac theory.

It remains to be proved that the same result holds for positive molecular ions. For ions, $\Delta\varphi$ extends over a finite volume. On the surface of this volume the electron density vanishes ($\Delta\varphi = 0$) in the Thomas-Fermi model, or assumes the minimum value ($\Delta\varphi = \kappa^3$ with $\Delta\varphi = 0$ outside the surface) in the Thomas-Fermi-Dirac model. But in contrast to the case of neutral structures, φ will not be constant outside the region where $\Delta\varphi \neq 0$. For the ionic case it is necessary to introduce a constant φ_0 for all ions (or atoms) and to use $\varphi - \varphi_0$ instead of φ in Eqs. (1) and (5). On the surface of these structures the quantity $\varphi - \varphi_0$ vanishes. If a single value φ_0 is used and if this value is positive (i.e., greater than the value φ assumes at infinity where we set $\varphi = 0$), then we are talking about an assembly of positive ions with no neutral structures present.

It is actually customary to use a different potential φ_l for the surface of each ion l and adjust these potentials in such a manner as to make the integrated charge density equal to a multiple of the elementary charge on each of the separate atoms, molecules and ions. From the point of view of the statistical model, this procedure is not quite consistent. In the following, a proof of the instability of ions is given only for the case where the potentials on the surfaces of all structures are equal to φ_0.

First, we point out that our lemma can be generalized for ions: If a localized infinitesimal positive charge is added and no compensating electrons are introduced the change in φ is everywhere positive definite. To show this we shall add an infinitesimal localized ζ and an amount of electrons which will have the result that we wind up with unchanged value of φ_0. Under these conditions the quantity $\varphi - \varphi_0$ will behave in the same way in which φ behaved in neutral atoms or molecules of limited extension in the Thomas-Fermi-Dirac model. Thus, $\varphi - \varphi_0$ increases everywhere except on the boundaries where it will remain unchanged. The same can be stated about φ since φ_0 has remained unchanged.

As a second step we shall change the number of electrons in such a way as to return to the total number of electrons that were found before ζ had been added. If one adds electrons to a solution of the statistical equation for ions, then in the new solution the quantity $\Delta\varphi$ increases everywhere. Indeed, negative values of $\Delta\epsilon$ can occur only in a bounded region. If we set ϵ equal to the change of $\varphi - \varphi_0$, use of Eq. (4) and the reasoning given subsequent to that equation show that such a region cannot exist. The increase of the negative charge density decreases the potential φ in all locations.

Furthermore, the addition of a positive charge, without adding electrons will surely increase φ_0. Otherwise more energy will be expended if we added ζ first and afterward an equal charge in electrons, than if we proceeded in the opposite order. The original addition of ζ has therefore increased φ_0, and we see that in our first step electrons had to be added to keep φ_0 constant. In our second step, therefore, electrons must be removed. This increases the value of φ at every position. Since in our first step we did not decrease φ anywhere our lemma is proved.

To proceed with our proof we shall consider a neutral structure with the same number of electrons as the ionic structure we want to investigate. This will be done—for the sake of comparison—both for the molecular ion and the separate atomic ions. After this we shall add successively localized infinitesimal charges ζ without adding electrons, but allowing electrons to redistribute themselves so as to maintain the same value φ_0 on all ions. It follows from our lemma and from a reasoning similar to the one given for neutral structures that in the process in which the molecular ion is built up, higher values of φ are encountered in each step and correspondingly more energy is required than in the process in which the atomic ions are being built. There is only one point in which this phase of the proof is different for the ions: After each addition of ζ, no electrons are added but we merely allow the electrons to readjust to the new positive charge distribution. But this readjustment (like the addition of electrons in the neutral case) adds only quadratic infinitesimal terms to the energy since the statistical models can be derived from a variational principle.

Therefore, we can say that a molecular ion in the statistical theories is less stable than the corresponding separate atomic ions, provided it is assumed that the electrons are so distributed in the latter case as to make the ionization potential φ_0 equal for all atomic ions.

If that last condition is dropped, one can easily construct appropriate examples in which the molecular ion in the statistical theory is more stable than atoms and atomic ions separated at infinite distances. For example, in the Thomas-Fermi-Dirac theory we can bring an ion into the neighborhood of a neutral atom. During this process we expend no work against a Coulomb repulsion, but polarization terms lower the energy. In the end the structures coalesce with a net lowering of energy. The same counterexample does not work in the Thomas-Fermi case because for this model neutral structures extend to infinity. But in this case we can consider an atomic ion with a low value of Z and exceedingly low difference between positive and negative charges. Such a structure will have a high polarizability. If we now bring up a bare nucleus of very great charge Z' the effect of polarizability will again outweigh the effect of the electrostatic repulsion. Indeed, the former is proportional to $(Z')^2$, whereas the latter increases only as the first power of Z'.

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Critique of the Heitler-London Method of Calculating Spin Couplings at Large Distances

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1. INTRODUCTION

A. Scope of the Present Paper

FOR a third of a century the concept of exchange coupling of two or more non-singlet atoms has occupied a prominent place in theories of molecular binding and of magnetism. This concept, born in the Heitler-London theory[1] of the chemical bond, was applied by Heisenberg[2] in his celebrated theory of ferromagnetism, and soon received a very appealing formulation in terms of spin vectors at the hands of Van Vleck[3] and Møller.[4] Although the "spin Hamiltonian" resulting from this formulation has continued to be used in much—even most—theoretical work on magnetism, grave doubts as to its validity have been expressed,[5,6] and various papers have attempted to disprove it, justify it, or test it.[7] The object of the present paper is to clarify the status of the spin Hamiltonian and of the Heitler-London method of calculating the constants entering into it for the limiting case to which the original derivations were intended to apply, namely, the case of well-separated atoms. We shall give a rigorous justification of the concept of a spin Hamiltonian, a physical picture of the virtues and limitations of the Heitler-London approach, and a prescription, which may even be practical in simple cases, for exact *a priori* calculation of the limiting exchange coupling.

It should be emphasized at once, however, that the arguments to be presented here are of more value to the world of pure thought than to the world of magnetic phenomena. For they are based, as we have implied, on the assumption that the wave functions of neighboring atoms overlap only slightly, and this is almost never true in molecules and solids. It has, of course, sometimes been supposed that the coupling of the atomic spins of unfilled $3d$ or $4f$ shells can be calculated by applying the Heitler-London method to the wave functions of these shells alone, ignoring the valence electrons responsible for chemical or metallic binding. If this were so, the assumption of weak overlap of neighbors would indeed be justified in many, though not all, cases. But in recent years it has become clear that the valence electrons just mentioned usually play a vital role in the coupling of the spins of neighboring atoms, via the indirect exchange[8] and superexchange[9] mechanisms. In metals, moreover, it may often happen that even the electrons responsible for ferro- or antiferromagnetism must be treated as itinerant, rather than tightly bound to their atoms.[10]

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[1] W. Heitler and F. London, Z. Physik **44**, 455 (1927).

[2] W. Heisenberg, Z. Physik **49**, 619 (1928).

[3] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932).

[4] C. Møller, Z. Physik **82**, 559 (1933).

[5] J. C. Slater, Revs. Modern Phys. **25**, 199 (1953).

[6] G. Heber, Fortschr. Physik **1**, 707 (1954).

[7] For a general review of this and other topics in the theory of direct exchange see C. Herring, "Theory of Direct Exchange" in *Magnetism* edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published).

[8] See the review by T. Kasuya in *Magnetism* edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published).

[9] See the review by P. W. Anderson, "Exchange in Insulators: Superexchange, Direct Exchange and Double Exchange," in *Magnetism* edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published).

[10] See the review by C. Herring, "Exchange Interactions Among Itinerant Electrons," in *Magnetism* edited by G. Rado and H. Suhl (Academic Press Inc., New York, to be published).