cillation has more of the character of a sound wave (with dispersion relation $\omega \simeq C_s k$). We believe that the divergent integral for W and the continuous rather than discrete frequency spectrum are faults of the fluid model. It is our conjecture, although we have no proof for it, that if Eq. (1) could be solved, a discrete frequency spectrum and a finite value of W would be found. In order to investigate further the error involved in our calculation of W, we have calculated

$$W_E = \int d^3x \frac{|\vec{E}|^2}{8\pi} < W . \qquad (30)$$

This integral is convergent and should be less than the true value of the energy. Therefore the value of γ calculated with W_E will be greater than the previous value by the factor W/W_E. Although this factor could become quite large (its largest value was 1.6×10^3 for $Z = 92$ and $\Omega = 2.756$), in no case was the value of γ/ω above unity.

Fortunately, our conclusion depends only on the order of magnitude of γ/ω. It seems very unlikely that elimination of the sources of error noted would change γ/ω by the orders of magnitude necessary to negate the conclusion that weakly damped plasma oscillations can exist in atoms.

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Electron Densities for Homonuclear Diatomic Molecules from the Thomas-Fermi-Dirac Theory

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Electron densities are calculated from approximate solutions to the Thomas-Fermi-Dirac equation for homonuclear diatomic molecules. The accuracy of expectation values calculated from these densities is assessed. In general, one obtains fair agreement with self-consistent-field and experimental results, but this is insufficient when a property is a difference between electronic and nuclear contributions. An important example is the Hellmann-Feynman force on a nucleus, the net force necessarily being repulsive, as for closed-shell atoms. Force and energy results for such a situation are compared with experiment. Finally, it is shown that a modified theory, previously applied to atoms, gives improvement in expectation values depending on the electron density near the nuclei.

I. INTRODUCTION

Quantum-statistical theories[1] such as the Thomas-Fermi-Dirac (TFD) theory lead to an integrodifferential equation for the electron density. Individual electrons are not treated, so the difficulty of the calculation is independent of the number of electrons, in contrast to the usual quantum-mechanical approaches. There was considerable interest in such calculations for atomic systems, but the success of self-consistent-field (SCF) calculations has led to a relative lack of interest in

TFD and related methods here. However, it appears now that, for molecules of even moderate size, SCF calculations will be too difficult for the near future. Thus, it seemed of interest to explore the usefulness of TFD calculations for molecules.

We here report some results for the simplest cases: homonuclear diatomics. We are interested in getting an idea of how accurate are the electron densities obtained, by comparing expectation values for various operators with SCF and experimental results. The calculation of the density is discussed in Sec. II, and the results for expectation values are given in Sec. III. From the atomic work, it is known that the attractive simplicity of the calculation is to be balanced against large inaccuracies in certain results due to breakdown of the assumptions of the theory very far from and very close to the nucleus. Many attempts have been made, and continue to be made, to alleviate this problem. A simple modification of the theory has led to great improvements in expectation values for atomic calculations. Its application to molecules is discussed in Sec. IV.

Previous molecular calculations seem to have been primarily concerned with the energy. The best TFD calculation for a molecular system known to us is that of Sheldon[2] for N_2. Other work on diatomics used the Thomas-Fermi theory, wherein exchange is not included. Hund[3] treated the Thomas-Fermi problem for N_2 and F_2 by a variational method, while Glazer and Reiss treated ICl and the CH bond of methane[4] by a relaxation method like the one we use here, and computed dipole moments. The most complete work is that of Townsend and Handler,[5] who solved the Thomas-Fermi equation for homonuclear diatomics by a relaxation procedure. It may be shown that, for the Thomas-Fermi theory, only one parameter need be specified (rather than both the nuclear charge Z and internuclear distance R). Thus, Townsend and Handler give a table of expectation values of operators entering the Hamiltonian for several values of this parameter. For a particular choice of Z, each corresponds to a different value of R, so that the energies for several different internuclear distances may be obtained.

The variation of energy with internuclear distance is of great interest in many of the above investigations. It now has been shown[6] that these theories cannot lead to a bound molecule, so that the energy decreases monotonically with increasing R. Equivalently, the net force on a nucleus, which is calculable from the electron density, is always positive (repulsive). It is suggested that the theory is valid for the interaction of rare-gas atoms, which is purely repulsive. Calculations of forces and energies for such a case are given at the end of Sec. III.

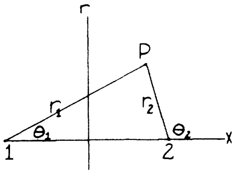

FIG. 1. Cylindrical coordinate system for diatomic molecule calculation. $\xi^{-1} = r_1^{-1} + r_2^{-1}$. $\eta = \cos\theta_1 + \cos\theta_2$.

II. TFD EQUATION FOR HOMONUCLEAR DIATOMICS

Our calculation follows essentially the method given by Sheldon.[2] The coordinate system used, which takes advantage of the symmetry and general characteristics of the solution, is defined in terms of the usual cylindrical coordinates in Fig. 1. The nuclei are at 1 and 2, the internuclear distance R being equal to $2a$. Instead of x and r one uses

$$\eta = \cos\theta_1 + \cos\theta_2 \ , \qquad (1)$$

$$\xi = (r_1^{-1} + r_2^{-1})^{-1} \ . \qquad (2)$$

For the homonuclear case it suffices to consider $x > 0$ or $0 < \eta < 2$. We go over to a system of units in which all distances are measured in units of a and the electronic charge and mass are unity. The TFD theory provides a relation between the potential V and the electron density ρ at each point in space. Sheldon introduces the function u such that u^2/ξ is proportional to $V + (32\pi^2)^{-1}$. The density is given as

$$\rho = (1/3\pi^5 a_0^3)[u/(a\xi)^{1/2} + 1]^3 \ . \qquad (3)$$

Equation (3), in conjunction with the Poisson equation which also relates V and ρ, leads to a differential equation for u. In the present coordinate system, it is

$$\frac{\partial^2 u^2}{\partial t^2} - \frac{\partial u^2}{\partial t} + \left(\frac{\partial}{\partial \eta}\frac{r^2}{\xi^2}\right)\frac{\partial u^2}{\partial \eta} + \left(\frac{r^2}{\xi^2}\right)\frac{\partial^2 u^2}{\partial \eta^2} = F \ . \qquad (4)$$

Here, $t = \ln(\xi)$ and

$$F = \frac{8}{3\pi^2} g a^3 \xi^3 \left(1 + \frac{u}{(a\xi)^{1/2}}\right)^3 , \quad u > \tfrac{1}{4}(a\xi)^{1/2} \qquad (5a)$$

$$F = 0, \qquad u < \tfrac{1}{4}(a\xi)^{1/2} \qquad (5b)$$

where g is the metric, the volume element being

$$d\tau = g\xi^2 d\xi \, d\eta \, d\varphi \ . \qquad (6)$$

(There is a discontinuity of the density which is a necessary consequence of the TFD theory.) Near a nucleus, the potential must approach the Coulombic potential, and this leads to the boundary condition

$$u \to (2Z)^{1/2}\pi \ \text{as} \ t \to -\infty \ . \qquad (7)$$

The differential equation is treated by transforming it to a finite difference equation by the usual formulas. The grid of points in η is equally spaced from $\eta = 0$ to $\eta = 2$. The range of t and its definition mean that equal spacing is not appropriate; the points go from t_0 (negative enough so that the density for $t < t_0$ may be taken as the TFD atomic density) to t_c such that $t = t_c$ falls outside the surface of discontinuity of ρ, which we denote as $t_b(\eta)$. Sheldon[2] gives the difference equations, and our formulas agree with his except for one case, the first derivative of u^2 with respect to t. Letting k index the t points and i index the η points, we put

$$\left(\frac{\partial u^2}{\partial t}\right)_{ik} \rightarrow \frac{(u_{i,k+1}^2 - u_{i,k}^2)\Delta t_{k-1/2}}{\Delta t_{k+1/2}(\Delta t_{k+1/2} + \Delta t_{k-1/2})} + \frac{(u_{i,k}^2 - u_{i,k-1}^2)\Delta t_{k+1/2}}{\Delta t_{k-1/2}(\Delta t_{k+1/2} + \Delta t_{k-1/2})} . \qquad (8)$$

Here, $\Delta t_{k+1/2} = t_{k+1} - t_k$.

The finite difference equation for the point (i, k) is

$$f(u_{i,k}, u_{i,k+1}, u_{i,k-1}, u_{i+1,k}, u_{i-1,k}) = 0 . \qquad (9)$$

The solution is obtained by a relaxation method. We go over the grid of points, adjusting the value of u in each case according to

$$u_{i,k} \rightarrow u_{i,k} - \alpha f \bigg/ \left(\frac{\partial f}{\partial u_{i,k}}\right) , \qquad (10)$$

repeating the process until the u's no longer change. When $\alpha = 1$, the new value of $u_{i,k}$ would make $f = 0$ if f were linear in $u_{i,k}$. Actually, the parameter α may be chosen to optimize the rate of convergence of the method, and Sheldon[2] shows $0 < \alpha < 2$ is permissible. We start by putting $u = \frac{1}{4}(a\xi)^{1/2}$ for all points on $t = t_c$. As the integration proceeds, we put $u_{i,k} = \frac{1}{4}(a\xi_k)^{1/2}$ whenever the corrected $u_{i,k}$ from (10) falls below $\frac{1}{4}(a\xi_k)^{1/2}$. (In the computation of expectation values, discussed below, we put $\rho = 0$ for such points.) To satisfy the boundary condition (7), we use the fact that, close to a nucleus, the solution of the TFD equation becomes identical to that for the neutral atom of that nuclear charge. Thus, we set the values of u for the surface $t = t_0$ using atomic TFD solutions at the outset.

The surface $t_b(\eta)$ is not very well defined by this procedure. The error in the computed norm (see below) reflects this in part. Sheldon indicates how one may use this known error to correct other expectation values. It seems to us, however, that the solution to Eq. (4) is not uniquely specified with these boundary conditions [u given for $t = t_0$ and $u = \frac{1}{4}(a\xi)^{1/2}$ for $t > t_b$], but that an infinite number of solutions exist, corresponding to a range of possible slopes $\partial u/\partial t$ on t_0. One really should impose continuity of the slope $\partial u/\partial t$ at t_0. We believe that the character of the solutions (assuming they behave like those for atoms) is what saves things, for an initial slope slightly too high leads to a solution which starts to rise rapidly before it can intersect $u = \frac{1}{4}(a\xi)^{1/2}$, while one which is slightly too low intersects $u = \frac{1}{4}(a\xi)^{1/2}$ too quickly to satisfy the normalization condition.

III. EXPECTATION VALUES FOR HOMONUCLEAR DIATOMICS

We are interested in the expectation values of various functions of the coordinates. Letting F be such a function, we have

$$\int F\rho\, d\tau = a^3 \int_0^{2\pi} d\varphi \int_{-2}^{2} d\eta \int_0^{\infty} d\xi\, (\xi^2 F\rho g)$$

$$= 4\pi a^3 \int_0^{2} d\eta \int_{-\infty}^{\infty} dt\, (\xi^3 F\rho g) , \qquad (11)$$

with integration now limited to the quadrant $x > 0$, $r \geq 0$ of the plane in Fig. 1. The density is expressed in terms of u and the trapezoid rule is used to carry out the integration. The integral over t is actually carried out from $t = t_0$ and not $t = -\infty$, with the contribution from $t < t_0$ being evaluated separately using the atomic TFD function. Letting t_b be the maximum value of t for which ρ is nonzero (t_b should really depend on η) and letting $\Delta t_{b+1/2}$ and $\Delta t_{-1/2}$ be zero, the integral is approximated as

$$\int F\rho\, d\tau = \frac{2\Delta\eta a^3}{3\pi^4} \sum_{i=0}^{n_e} \sum_{k=0}^{b} (\Delta t_{k+1/2} + \Delta t_{k-1/2}) \times W_i (u_{i,k} y_k + 1)^3 \xi_k^3 g_{ik}^3 F_{ik} . \qquad (12)$$

Here, $y = (a\xi)^{-1/2}$.

We first discuss results for N_2 at internuclear distances of 2.076 and 6 Bohr radii (the latter is close to the separated atom limit) and for F_2 at $2.74a_0$. The internuclear distances for the first and last are close to the experimental potential minima. We will be comparing expectation values with those from SCF calculations and, in some cases with the results of Sheldon[2] and of Townsend and Handler.[5] Ten η points ($\Delta\eta = \frac{2}{9}$) were used and about 20 points in t. The spacing of the t points was smaller near t_0, near t_b, and near $t = \ln\frac{1}{2}$, which is a singular point in this coordinate system. About fifty iterations sufficed to get values of u constant to 0.001. A complete calculation for a given value of a and Z took about $3\frac{1}{2}$ min on an IBM 360.

Some molecular properties dependent on the electron density are (a) the electron-nuclear attraction energy and diamagnetic shielding, which require $\langle 1/r_1 \rangle$; (b) the diamagnetic susceptibility and quadrupole moment, or $\langle a^2 x^2 \rangle$ and $\langle a^2 r^2 \rangle$; and (c) the Hellmann-Feynman force on the nuclei, which means $\langle \cos\theta_1 / r_1^2 \rangle$ or $\langle -\cos\theta_2 / r_2^2 \rangle$. Properties (a) and (c) depend on the behavior of the density near the nuclei, and (b) depends on its behavior at the periphery of the molecule. The Hellmann-Feynman force is notoriously difficult to calculate accurately, even for quantum-mechanical densities. In addition to these expectation values, we calculate the normalization $\langle 1 \rangle$, which must be equal to the number of electrons for the exact solution, as a check on accuracy.

In Tables I–VI, we have added to the expectation values calculated from the solution to (4) contributions for the density for $t < t_0$, using the atomic density. For the normalization, we must add

$$2\mathcal{J} = 2 \int_0^{r_0} 4\pi r^2 \, dr \, \rho_{\mathrm{TFD}} = 2Z \int_0^{x_0} x\psi'' \, dx$$

$$= 2Z[x_0\psi'(x_0) - \psi(x_0) + 1] \quad . \tag{13}$$

Here, t_0 is negative enough so the surface $t = t_0$ consists of two circles around the nuclei of radius r_0; x is the dimensionless coordinate of the TFD theory and is given by

$$x = r/\mu \ , \tag{14}$$

with

$$\mu = \tfrac{1}{4}(3\pi)^{2/3}(2Z)^{-1/3}a_0 \ ;$$

and ψ is the solution to the usual atomic TFD equation. The contribution of this density to $\langle r_1^{-1} + r_2^{-1} \rangle$ is

$$2\mathcal{J}(2a)^{-1} + 2 \int_0^{r_0} 4\pi r^2 dr \, \rho_{\mathrm{TFD}} r^{-1}$$

$$= \mathcal{J}/a + 2Z\mu^{-1} \int_0^{x_0} dx \, \psi''$$

$$= \mathcal{J}/a + 2Z\mu^{-1}[\psi'(x_0) - \psi'(0)] \ . \tag{15}$$

The first term is the contribution of density on one nucleus to the potential at the other. The second term here is actually much more important than the first and represents the contribution of density to the nucleus on which it is centered. The contribution to $\langle r^2 \rangle$ is taken as zero, since the density lies on the internuclear axis, while the contribution to $\langle x^2 \rangle$ is $2\mathcal{J}z^2$. If the density within t_0 can be considered spherically symmetric, its contribution to the Hellmann-Feynman force would be $2\mathcal{J}/(2a)^2$; that is, the density centered on a nucleus exerts no force on that nucleus and behaves like a point charge with respect to the other.

Since the force is sensitive to the density near the nucleus, we thought it advisable to make some estimate of the effect of polarization here. The calculated expectation value f,

$$f = \langle r_1^{-2} \cos\theta_1 - r_2^{-2} \cos\theta_2 \rangle \ , \tag{16}$$

should be increased by $2[Z(2a)^{-2} - \tfrac{1}{2}f]\mathcal{J}/Z$, as shown in the Appendix.

In Table I we give results from our calculation and from Sheldon's[2] at $R = 2.076a_0$, and compare with what is obtained from an SCF calculation.[7] The SCF calculation is actually for $R = 2.038a_0$, but the errors in the present method are generally larger than the changes due to the altered R. Just as for atoms, the expectation value $\langle r_1^{-1} + r_2^{-1} \rangle$ is about $\frac{1}{3}$ too high, due to the breakdown of the assumptions of TF and TFD near the nucleus (the density actually goes infinite there). It is this behavior that we will be able to correct in Sec. IV. Townsend and Handler's Table I allows us to compute the Thomas-Fermi result for this case: 54.5. The inclusion of exchange allows the electrons to cluster more closely about the nuclei, so the TFD result is even worse than the TF for this property. The incorrect behavior of the theory for large distances, as evidenced by the discontinuity in ρ, tends to make expectation values like $\langle a^2x^2 \rangle$ and $\langle a^2r^2 \rangle$ too high. The errors in these for N_2 are less than might have been expected, but this may be a coincidence: Things are much worse for F_2 (see Table II). In fact[8] one finds similar luck for Ar among the rare-gas atoms. It must also be noted that these expectation values are extremely sensitive to the location of the boundary $t_b(\eta)$, and this is certainly not being calculated correctly by the present method as we

TABLE I. N_2, $R = 2.076a_0$ (all expectation values in atomic units).

Expectation value	This calculation	Sheldon	Nesbet[a]
$\langle 1 \rangle$	14.026	13.89	14.000 (exact)
$\langle r_1^{-1} + r_2^{-1} \rangle$	57.28	57.15	43.29
$\langle a^2x^2 \rangle$	24.22	···	23.60
$\langle a^2r^2 \rangle$	18.55	···	15.49
$\langle r_1^{-2} \cos\theta_1 - r_2^{-2} \cos\theta_2 \rangle$	3.00	2.93, 2.97[b]	3.25[c]

[a] Reference 7. These expectation values are actually for $R = 2.068a_0$.

[b] The expectation value was not directly calculated by Sheldon, but derived from other expectation values via the virial theorem (first result) or from the variation of kinetic energy with distance (second result).

[c] This is not the expectation value from Nesbet's wave function, but is obtained from the fact that the electronic and nuclear contributions to the force must balance for the equilibrium nuclear configuration.

TABLE II. F_2, $R=2.74a_0$ (all expectation values in atomic units).

Expectation value	This calculation	Wahl[a]
$\langle 1 \rangle$	18.005	18.000 (exact)
$\langle r_1^{-1}+r_2^{-1} \rangle$	76.501	59.86[b]
$\langle a^2x^2 \rangle$	45.27	38.66
$\langle a^2r^2 \rangle$	25.63	13.99
$\langle r_1^{-2}\cos\theta_1 - r_2^{-2}\cos\theta_2 \rangle$	2.28	2.40[c]

[a] Reference 9. This calculation is actually for $R=2.68\alpha_0$.

[b] C. W. Kern and W. N. Lipscomb, J. Chem. Phys. 37, 260 (1962).

[c] This is not the expectation value from Wahl's wave function, but is obtained from the fact that electronic and nuclear contributions to the force must balance for the equilibrium nuclear configuration.

have noted. It turns out that by varying the grid points in the region of $t_b(\eta)$ one does not much affect expectation values other than $\langle a^2x^2 \rangle$ and $\langle a^2r^2 \rangle$. These are however changed by as much as several a_0^2. The error in the last property is smaller than expected, but note that the part of the electron density which is spherically symmetric about a nucleus makes no contribution to the force on the nucleus. In this case, $\mathscr{s} \sim 0.0757$. Then the polarization correction, estimated according to our previous scheme, is less than $0.01a_0^{-2}$.

In Table II, we give the corresponding result for F_2, at an internuclear distance of $2.74a_0$, and compare it to a calculation by the SCF method.[9] Here, $\mathscr{s}=0.161$, and the polarization contribution to the force is again less than 0.01. The expectation values behave like those of Table I. Finally, Table III gives results for N_2 at $R=6a_0$. The results from the quantum-statistical calculations are compared with results for separated atoms. The atoms are not quite separated in the quantum-statistical calculations, since their charge distributions are not nonoverlapping. The cutoff for the electronic density is at about $4a_0$ from the nuclei.

While Sheldon[2] and Hund[3] gave no expectation values for $\langle x^2 \rangle$ and $\langle r^2 \rangle$, Bonet and Bushkovitch[10] estimated the TFD diamagnetic susceptibilities, proportional to $\langle x^2 \rangle + \langle r^2 \rangle$, for Hund's N_2 density. This TF density was corrected for exchange and correlation by cutting it off at a finite distance from the nuclei, like a TFD density, and rescaling to preserve normalization. This was done by analogy with TF and TFD results for atoms. They found $\langle a^2x^2 \rangle + \langle a^2r^2 \rangle = 42.55a_0^2$, to be compared to our result (Table I) of 42.77. Nesbet's result for this quantity is 39.09; taking this as correct means our error is only 9%. For F_2, we differ from Wahl's results for the diamagnetic susceptibility relative to the molecular midpoint by 31%.

The situation for the electronic contribution to the molecular quadrupole moment may be even worse, since this depends on the difference of expectation values $\langle a^2x^2 \rangle - \frac{1}{2}\langle a^2r^2 \rangle$. It turns out that our results agree to about 6% for N_2 and F_2, but for some other case the errors in the two quantities could as well add as cancel. But even a "good" value here is not enough since the molecular quadrupole moment is itself a difference between a nuclear and an electronic contribution. The nuclear contribution is $2Za^2$ (we are taking the molecular midpoint as origin throughout) and is rather close to the electronic contribution, so that we calculate in both cases quadrupole moments of the wrong sign as well as magnitude. A similar problem arises in the electronic force on a nucleus $\frac{1}{2}f$. When this is subtracted from the force due to the other nucleus $Z/(2a)^2$ the errors of 10% or so in f become all important. One obtains a zero or positive force for all our three cases.

Sheldon,[2] who remarked that the energy of the N_2 system increased monotonically as the internuclear separation decreased, explained it in terms of the rapidly rising kinetic energy. He suggested that the TFD theory actually describes the atoms as well as the molecule as closed-shell systems and so never gives rise to covalent bonding. Chem-

TABLE III. N_2, $R=6.0a_0$ (all expectation values in atomic units).

Expectation value	This calculation	Sheldon	TFD atoms[a]	SCF atoms[a]
$\langle 1 \rangle$	13.977	13.95	...	14 (exact)
$\langle r_1^{-1}+r_2^{-1} \rangle$	52.85	53.05	53.02	39.06
$\langle a^2x^2 \rangle$	125.88	...	...	68.32
$\langle a^2r^2 \rangle$	20.64	...	...	16.16
$\langle r_1^{-2}\cos\theta_1 - r_2^{-2}\cos\theta_2 \rangle$	0.39	0.39, 0.38[b]	0.39	0.39

[a] Assuming noninteracting atoms, i.e., superposition of atomic densities. $\langle r^{-1} \rangle$ for isolated TFD atoms is given by L. H. Thomas, J. Chem. Phys. 22, 1758 (1954).

[b] Not directly calculated (cf. preceding tables).

ical bonding is of course a periodic phenomenon, which strictly quantum-statistical theories cannot reproduce. Because of the scaling which is possible in the TF theory for a neutral homonuclear molecule (multiplication of Z by k and R by $k^{-1/3}$ multiplies the energy by $k^{7/3}$), the potential curves for all such molecules have the same shape. As was emphasized by Teller,[6] if the molecule with nuclear charges Z_1 has a minimum for $R=R_e$, scaling would produce a minimum at $R=(Z_2/Z_1)^{-1/3}R_e$ for the molecule with nuclear charges Z_2, the binding energy being multiplied by $(Z_2/Z_1)^{7/3}$. It is probably just as well that no minima occur. The TFD results follow the TF results because, as observed by Sheldon, the change in exchange energy with R is of minor importance.

Several years after Sheldon's calculations, Teller[6] was able to show in general that the energy of a molecular system treated by the TF or TFD theory is never lower than the energy of the separated atoms. Subsequently, Balazs[11] showed that any theory in which the electron density at a point is a function only of the electrostatic potential at that point makes the net force on a nucleus of a homonuclear diatomic molecule positive. (The Weizsäcker-type kinetic-energy correction makes the potential depend on derivatives of the density as well as the density. Balazs shows that this type of theory leads to a net attractive force for sufficiently large internuclear distance and hence to stable molecules. However, it still seems to us that any theory which takes no account of individual electrons must give similar behavior for N_2, F_2, and Ne_2 with respect to molecular binding.) The equivalence of the force and energy points of view is assured by the Hellmann-Feynman theorem.[12]

An interesting approach was taken by Townsend and Keller,[13] who corrected the TF energies of Townsend and Handler[5] for exchange and for the breakdown of the statistical theories close to the nuclei by a method used for atoms by Scott.[14] To correct for the poor behavior near the nuclei, it is noted that, since the potential seen by the electrons here is essentially the pure Coulombic potential of the nucleus, the correction to the energy should be about the same as for the situation where the interelectronic repulsion is neglected. Thus, one computes, by TF and by quantum mechanics, the energy for the system differing from the one in question by the omission of the interelectronic repulsion terms from the Hamiltonian (the quantum-mechanical energy is simply a sum of scaled H_2^+ energies). Then the difference $E_{TF}-E_{qm}$ is subtracted from the TF energy for the original system. The use of E_{qm} means some periodicity is introduced by the H_2^+ shell structure, and Townsend and Keller report[13] some slight binding at large R for Li_2, N_2, and Na_2, but none for the rare gases. This is interesting in light of the fact that the behavior of the electrons at the periphery of the molecule, which normally is associated with chemical properties, is not corrected.

Another possibility is to use a Weizsäcker-type correction. Gombás[15] has reported a binding energy of 10 eV for N_2 from such a calculation.

In any case, if the unmodified TFD or TF is to be used, only closed-shell systems should be treated. This could mean treating only the inner-shell electrons according to such a theory,[16] or one can consider a highly polar diatomic to be composed of closed-shell ions. Then the exchange repulsion may be treated according to the TFD theory, while the potential energy automatically includes a term corresponding to the ionic Coulombic attraction, and the result is a potential curve with a minimum.[17] This picture does not seem reasonable except for large R.

The question is whether it is really justified to apply the theory to the interaction of closed-shell systems. This may be tested by computation of the repulsive interaction potential between rare-gas atoms, a problem which has been investigated by Abrahamson and co-workers.[18] They did not solve the TFD equation directly, but employed two variational principles which lead to upper and lower bounds for the energy in the TFD approximation when an approximation to the TFD density is inserted. When a superposition of atomic TFD densities was used, the mean of the upper and lower bounds could be shown to differ from the correct TFD energy by less than 4%. Below, we shall compute the TFD energy, as well as the force, directly from the solution to the TFD equation for the Ar-Ar system.

The total energy is a sum of electronic kinetic energy K, interelectronic repulsion I, exchange energy U (a negative contribution), nuclear-electronic attraction V_{ne}, and internuclear repulsion V_{nn}. V_{ne} is just the nuclear charge times $\langle r_1^{-1}+r_2^{-2}\rangle$, V_{nn} is Z^2/R,

$$K=\tfrac{3}{10}(3\pi^2)^{2/3}\int d\tau\,\rho^{5/3}\ , \tag{17}$$

$$U=-\tfrac{3}{4}(3/\pi)^{1/3}\int d\tau\,\rho^{4/3}\ , \tag{18}$$

where ρ is the electron density. To compute I, we write it as

$$I=\frac{1}{2}\iint d\tau_1 d\tau_2\,\rho(\vec{r}_1)\rho(\vec{r}_2)|\vec{r}_1-\vec{r}_2|^{-1}$$

$$=-\frac{1}{2}\int d\tau\,\rho\ (\vec{r})\left(V-\frac{Z}{r_1}-\frac{Z}{r_2}\right)\ ,$$

since this is the interaction of the electron density with the electrostatic potential due to the other electrons only. In terms of u and in atomic units we have

TABLE IV. Ar-Ar (expectation values in atomic units).

R	$1a_0$	$2a_0$	$3a_0$
η	35.950	36.143	36.087
$-V_{ne}$	3746.3	3477.5	3368.2
K	1402.9	1383.2	1378.0
I	743.8	624.2	573.4
$-U$	61.2	58.9	58.1
V_{nn}	324.00	162.00	108.00
f	29.15	8.72	4.00
$5K+3V+6I+4U$	-6.4	-6.9	-6.6

$$I=-\frac{1}{2}\int d\tau\left(\frac{1}{2\pi^2}\frac{u^2}{a\xi}-\frac{1}{32\pi^2}\right)\rho-\tfrac{1}{2}V_{ne}\,. \tag{19}$$

It is not really necessary to compute all the expectation values directly, since Sheldon[2] showed

$$5K+3V_{ne}+6I+4U=-45\eta/32\pi^2\,, \tag{20}$$

where η is the integral of ρ over all space, theoretically $2Z$. Sheldon used (20) to determine I, but we employ it as a check on the expectation values and determine I from (19). From (17)-(19), it is easy to show that (20) holds for the contribution to the expectation values for $t>t_0$. The errors come from the atomic contributions, some of which are obtained by numerical integration and some from formulas like (15).

Table IV gives, for internuclear distances of 1, 2, and $3a_0$, the expectation values involved in the energy and the force. About 400 points were used in this calculation. The computed values of (20) are also given, as well as the computed values of η. We experimented with changing the numbers of integration points to estimate errors in the expectation values. While individual expectation values are good to a fraction of a percent, the errors in the energies are still large compared to what is of interest: the energy differences. The forces, energies, and energy differences are given in Table V. Abrahamson discussed a number of experimentally and theoretically determined interaction potentials for the Ar-Ar system (as well as for other pairs of rare-gas atoms), summarizing the results in Fig. 7 and Table II of his article. We take energy differences $E(2a_0)-E(a_0)$ and $E(3a_0)-E(2a_0)$ from his Table II, and slopes of dE/dR from his curve, which follows experimental results for this region of R. These are given in Table VI; unfortunately, only one significant figure could be read off for the slope.

Our energy differences and forces are consistent, as they must be for a correct solution to the TFD equation. There is a discrepancy with Abrahamson's results at larger R which is not too large to be accounted for by calculational errors on our part, as judged by the effect of changing the numbers of integration points. We conclude that accurate computation of relatively small energy differences is extremely difficult.

IV. MODIFIED CALCULATIONS

Many attempts have been made[19,20] to alleviate the incorrect behavior of the TFD density for large and small distances from the nuclei, due to the breakdown of the assumptions of the theory here. We suggested[21] that one could use a correct quantum-mechanical density close to a nucleus and join it to a density obtained from a quantum-statistical theory in other regions, thus avoiding the error due to use of the quantum-statistical approximations where they are poor. The poor behavior at large distance is left unchanged. The procedure is practical because the quantum-mechanical density near a nucleus of an atom is well represented by that of two noninteracting electrons moving in the nuclear Coulombic field. Physically, this is so because the Coulombic potential of the nucleus dominates all other interactions here. Thus, for the atomic case, we tried using such a density for $r<r_0$ (r is the distance from the nucleus) and a density obtained from TF or TFD for $r>r_0$.

For the TF case, we require continuity of the density ρ at r_0 together with normalization and proper behavior at infinity. The first two conditions fixed the value and slope of the TF function at r_0, so that the TF differential equation could be integrated outward. For some choice of r_0, the solution went smoothly to zero as r went to infinity, which determined r_0. For TFD, the function does not extend to infinity, and the outer boundary condition can be fulfilled for a range of values of r_0. To fix the value of r_0, we demanded, in addition, continuity of

TABLE V. Ar-Ar: energies and forces (atomic units).

R	$1a_0$		$2a_0$		$3a_0$
Energy	-1336.8		-1367.0		-1366.9
Force	61.7		2.5		0.0
Energy difference		-30.2		0.1	
Force, Ref. 18	60		5		0.6
Energy difference, Ref. 18		-38.4		-4.6	

TABLE VI. Modified TFD calculations (all expectation values in atomic units).

Z	7	9
R	2.076	2.74
t_0	−2.79	−3.29
g	0.27	0.14
$\langle 1 \rangle$	14.04	17.90
$\langle r_1^{-1}+r_2^{-1} \rangle$	42.98	57.48
$\langle a^2x^2 \rangle$	24.67	45.09
$\langle a^2r^2 \rangle$	18.97	23.70
f	2.91	2.24

$d\rho/dr$. The resulting densities were a considerable improvement on those obtained from the unmodified theories with respect to expectation values like $\langle r^{-1} \rangle$. Ashby and Holtzmann,[20] in a paper appearing after ours was submitted, gave similar arguments and suggested a similar modification. They treated the nonrelativistic and relativistic TF problems for atoms. The radial density for $r < r_0$ was taken of hydrogenic form

$$4\pi r^2 \rho = \alpha r^2 e^{-\beta r}\,, \tag{21}$$

with α and β two parameters to be determined. The chemical potential in the TF equation was allowed to vary in order to ensure normalization (we assumed it to be zero, the value for the unmodified theory). To determine the three parameters r_0, α, and β, a third condition was added to the continuity of ρ and $d\rho/dr$ at r_0: the continuity of the kinetic-energy density at r_0. Here, the quantum-mechanical kinetic-energy density was $-(\hbar^2/m)\psi\nabla^2\psi$ where the density ρ is equal to $2|\psi|^2$.

We now want to apply our method to the molecular TFD problem. This means that we assume for the electron density

$$\rho_A = 2(Z^3/\pi, e^{-2Zr} \quad \text{for } t < t_0\,, \tag{22}$$

where Z is the nuclear charge and r the distance to the closer nucleus. ρ_A is simply the density due to two 1s electrons. We may note that the condition

$$\left(\frac{d\rho}{dr}\right)_{r\to 0} = -2Z\rho(0)\,,$$

which must hold[22] for the true quantum-mechanical density, is automatically satisfied by (22), but not by (21) if β is not equal to $2Z$. In the TFD calculations described in Sec. III, we set the values of $u(t_0)$ in any case, so very little modification is required. Of course, t_0 must be small enough so the 1s density is a good approximation to the total atomic density here. This means that the radius of the circles corresponding to $t = t_0$ must be less than the first Bohr radius $Z^{-1}a_0$. When t_0 is determined by normalization (see below) this turns out to be the case.

We now obtain $u(t_0)$ from Eq. (3) using ρ_A:

$$u(t_0) = (e^{t_0}a)^{1/2}\left[(3\pi^5\rho_A)^{1/3} - 1\right] \tag{23}$$

and carry out the numerical integration over the rest of space. The joining point t_0 is fixed from the requirement that $\langle 1 \rangle$, the electron density integrated over all space, be equal to $2Z$. In the calculations of Sec. III, $\langle 1 \rangle$ served as a check of the accuracy to which the differential equation is integrated. We use the same integration points for the modified calculations. Now closeness of $\langle 1 \rangle$ to $2Z$ reflects how accurately t_0 is chosen. We have determined it to two decimals. It may be noted that the continuity of the electron density, but not its radial derivative, is assured by our procedure. In fact, the slope seems to be close to continuous across $t = t_0$, just as for the unmodified case.

The results of the modified calculations are given in Table VI, for F_2 and N_2. It may be seen that there is a great improvement in $\langle r_1^{-1}+r_2^{-1} \rangle$ over the unmodified calculations. Ashby and Holtzmann[20] report similar improvement in their method for $\langle r^{-1} \rangle$. We conclude that this simple expedient markedly improves the density close to the nuclei. It should be noted that, while the error in $\langle r_1^{-1}+r_2^{-1} \rangle$ goes from $\frac{1}{3}$ to a few percent, it is not simply a question of replacing a large contribution for $t < t_0$ by a small one. The density is modified for larger t as well, and we may expect other expectation values to be improved. Expectation values like $\langle a^2x^2 \rangle$ and $\langle a^2r^2 \rangle$ which depend on the density far from the nuclei are little changed (in fact they get slightly worse). In the light of what we have said above about the problems with this method with respect to these expectation values, these results may not be significant. The electronic force is changed little from its previous values. The polarization contribution to f is again small.

APPENDIX: CORRECTION TO FORCE DUE TO POLARIZATION OF ATOMIC DENSITY

Consider a spherically symmetric electron density $\rho(r)$, centered at a nucleus of charge Z and extending to a distance r_0 from the center. We suppose that the effect of an electric field E in the x direction can be represented as the displacement of $\rho(r)$ off the center by a distance d, so that it exerts a force on the nucleus in direction opposite to that exerted by E. To find d as a function of E, we minimize the expectation value of the energy. Since ρ is unchanged in size and shape and the kinetic-energy operator is invariant to a displacement of coordinates, we need consider only the change in potential energy. The displaced density is represented by $\rho(|r-d|)$. The change in energy is

$$\Delta\epsilon = -\int (Z/r)\rho(|r-d|)\,d\tau + E\int x\rho(|r-d|)\,d\tau$$

$$+\int (Z/r)\rho(r)d\tau .$$

With $q=\int_0^{r_0}\rho\, d\tau$, and using an expansion of r^{-1} in powers of distances from the new center, we find

$$\Delta\epsilon = Eqd + Z\int_0^{|d|}(r^{-1}-|d|^{-1})\rho(r)d\tau \quad \text{for } |d| < r_0$$

and

$$\Delta\epsilon = Eqd + Z\int_0^{r_0}(r^{-1}-|d|^{-1})\rho(r)d\tau \quad \text{for } |d| > r_0 .$$

We differentiate $\Delta\epsilon$ with respect to d and set the result equal to zero. In the first case, d is determined by

$$-Eq/Z = (d|d|)^{-1}\int_0^{|d|}\rho(r)d\tau$$

and in the second case by

$$-Eq/Z = (d|d|)^{-1}\int_0^{r_0}\rho(r)d\tau .$$

Both of these give $-Eq$ for the force exerted by the electrons on the nuclei, so the effect of the electric field is to reduce the field by a factor of $1-q/Z$. The field we are concerned with here is that due to the other nucleus and all the electrons outside t_0. The polarization effect has not been included in the tables; the correction to be added to the expectation value f is $2[Z(2a)^{-2}-\frac{1}{2}f]q/Z$. The second term is due to polarization, and the first is twice the force of a point charge q on a nucleus of charge Z at a distance $2a$.

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Annihilation of Positrons during Scattering

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The expression for the annihilation rate of positrons in scattering from atoms at an energy above the positronium (Ps) formation threshold is examined. A model describing the physical effects of annihilation is constructed and it is shown that no unexpected terms appear in the annihilation rate even when almost degenerate states of Ps are open channels. A previous calculation of positron-helium scattering is used to calculate the annihilation rate just above the Ps formation threshold where two competing effects complicate the expression. We conclude that the annihilation rate above threshold comes almost completely from the formation of real Ps.

I. INTRODUCTION

The annihilation of positrons during scattering by atoms is proportional to a contact interaction between the positron and each electron in the target.[1] This interaction[2] is small (of order α^3 or smaller)