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Interatomic Repulsive Potentials at Very Small and Intermediate Separations*†

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Using a minimal and a maximal principle, respectively, two approximate expressions for the interaction potential between atoms are given such that their mean, $\bar{U}(R)$, differs from the exact value, U_0, in the Thomas-Fermi-Dirac (TFD) approximation, by not more than 4% for the case of two-center system; and by not more than 14%, in the Thomas-Fermi (TF) approximation, for the case of a three-center system. The respective limits of applicability of these potentials are discussed, and some of their applications are pointed out.

I. INTRODUCTION

CONSIDERABLE interest attaches to interatomic repulsive potentials because of the important part they play in the study of gas scattering,[1] electrode sputtering,[2,3] radiation effects in solids,[4,5] and matter in the interior of stars.[6] Under these conditions, atoms approach each other much more closely than in solids under currently attainable pressures.[7] Theoretically, most of the interaction potentials that have been proposed, are relevant mainly to the vicinity of the equilibrium separation, but relatively little is known about these potentials at the considerably smaller separations referred to above.[8] It is the purpose of the present paper to develop a theoretical expression for this interaction energy at very small and intermediate internuclear distances.

The method for solving this problem is based, essentially, upon the application of a variational minimization-and-maximization principle, due to Firsov,[9] to the Thomas-Fermi statistical model of the atom.[10,11] While the Thomas-Fermi model was originally employed for calculating the central field of only one atom, the same model may also be used for calculating the interaction energy of two (or more) atoms, provided their separation is sufficiently small, and hence the overlap between their respective electron clouds sufficiently great, so that the statistical treatment is applicable.[9] The treatment to be given here, however, will be based on the more accurate Thomas-Fermi-Dirac statistical model of the atom.[12]

Inasmuch as the atomic interaction energy will be found to depend in a somewhat complicated manner upon the electron energy of the atomic system under consideration, our attention in the next three sections will be focused chiefly on this electron energy. Thus, in Sec. II, a functional H of the electron density ρ, and another functional H_1 of a certain function f are established. $H_0(\rho_0)$, the minimum of H, and $H_{10}(f_0)$, the maximum of H_1, are each equal to the exact electron energy in the TFD approximation. With the aid of these minimal and maximal principles, respectively, both upper and lower bounds can be determined for the relative error $\epsilon\equiv(H-H_0)/|H_0|$ in approximating H_0 by H, when H is calculated with a function ρ approximating the exact ρ_0. Similarly, upper and lower bounds can be determined for the mean relative error $\bar{\epsilon}\equiv[\frac{1}{2}(H+H_1)-H_0]/|H_0|$, when H_1 is calculated with a function f approximating the exact f_0.

In Sec. III, this formalism is applied to the TFD two-center problem. Here ρ_0 is approximated by simple superposition of the undistorted, exact single-center densities ρ_{01} and ρ_{02} of atoms 1 and 2, respectively; similarly, f_0 is approximated by superposition of the appropriate single-center functions f_{01} and f_{02}. The errors ϵ and $\bar{\epsilon}$ are then found to have upper bounds of less than 8% and 4%, respectively. As a second application, the three-center problem is treated in Sec. IV. A configuration in which the atoms occupy the vertices of an equilateral triangle is assumed. Here, analogously to the procedure followed in the two-center case, ρ_0 is approximated by the superposed exact single-center

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densities $(\rho_{01}+\rho_{02}+\rho_{03})$; and similarly, f_0 by $(f_{01}+f_{02}+f_{03})$. Evaluation of the upper bounds on ϵ and $\bar{\epsilon}$ gives less than 15% and 7.5%, respectively. In this case, however, the TF (rather than TFD) model was used in order to keep the work tractable. Essential formal and physical distinctions between the two models are indicated.

In Sec. V, the complete expressions for the interaction potentials $U(R)$, $U_1(R)$, and their average, $\bar{U}(R)$, are formed by adding the internuclear Coulomb term $Z_1Z_2e^2/R$ to $[H-H(\infty)]$, $[H_1-H_1(\infty)]$, and $\{\frac{1}{2}[H+H_1]-\frac{1}{2}[H(\infty)+H_1(\infty)]\}$, respectively. The symbols $H(\infty)$ and $H_1(\infty)$ represent the values of these functionals when the atoms comprising the system are infinitely far apart. Setting the exact TFD interaction potential $[Z_1Z_2e^2/R+H_0-H_0(\infty)]\equiv U_0(R)$, it is shown that, for an arbitrary number of nuclei, the relative errors $\epsilon_U\equiv(U-U_0)/U_0$ and $\bar{\epsilon}_U\equiv(\bar{U}-U_0)/U_0$ have respective upper bounds less than those on the corresponding errors ϵ and $\bar{\epsilon}$ defined above. Hence it follows that for a TFD two-center system, $\epsilon_U<8\%$, and $\bar{\epsilon}_U<4\%$; and for a TF three-center system (with equilateral triangle configuration), $\epsilon_U<27\%$, and $\bar{\epsilon}_U<13.5\%$. Firsov's[9] two-center TF potentials are shown to be obtainable from our three-center formulas as special cases, namely by letting the Z and ρ pertaining to one of the three atoms vanish.

A discussion of the results, indicating the limits of their applicability and outlining some of their further applications, is contained in Sec. VI.

II. TOTAL ELECTRON ENERGY IN THE TFD APPROXIMATION

A. Minimization Principle

The total electron energy of a system of interacting atoms, according to the Thomas-Fermi-Dirac (TFD) statistical model of the atom, is given by[6]

$$H=\kappa_k\int\rho^{5/3}dv+\tfrac{1}{2}e^2\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}dv'dv-e^2\int\sum\frac{Z_i}{r_i}\rho dv-\kappa_a\int\rho^{4/3}dv, \quad (1)$$

where the first term on the right represents the kinetic energy of the electrons; the second, the electron interaction energy; the third the interaction energy between the electrons and the nuclei; and the fourth, the electron exchange energy. Also,

$$\begin{aligned}\kappa_k&=\tfrac{3}{10}(3\pi^2)^{2/3}e^2a_0\simeq2.9e^2a_0;\\ \kappa_a&=\tfrac{3}{4}(3/\pi)^{1/3}e^2\simeq0.74e^2;\\ e&\equiv|e|;\end{aligned}\quad (2)$$

and a_0, ρ, Z_ie, r_i, respectively, denote the radius of the smallest Bohr orbit in hydrogen; the number of electrons per unit volume; the nuclear charge of the ith atom; the distance to the ith nucleus. Here and henceforth, the nuclei are assumed to be either held fixed, or else, moving so slowly that the adiabatic approximation is justified.

Extremalizing H by variation with respect to ρ, subject to the normalization condition

$$e\int_\Omega\rho dv=Ne, \quad (3)$$

where N is the total number of electrons in the volume Ω, and introducing a Lagrangian multiplier V_0 gives

$$(5/3)\kappa_k\rho_0^{2/3}+e^2\int\frac{\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}dv'-e^2\sum\frac{Z_i}{r_i}-\tfrac{4}{3}\kappa_a\rho_0^{1/3}+V_0e=0, \quad (4)$$

where, from TFD theory,[6]

$$V_0=\kappa_a^2/4\kappa_ke>0. \quad (5)$$

Substitution for $\kappa_k\rho_0^{2/3}$ from (4) into (1) then gives for the extremum of H,

$$H_0=-\tfrac{1}{10}e^2\int\int\frac{\rho_0(\mathbf{r})\rho_0(\mathbf{r}')}{|r-r'|}dv'dv-\tfrac{2}{5}e^2\int\sum\frac{Z_i}{r_i}\rho_0dv-\tfrac{1}{5}\kappa_a\int\rho_0^{4/3}dv-\tfrac{3}{5}V_0e\int\rho_0dv, \quad (6a)$$

or, eliminating also the double integral by means of (4),

$$H_0=\tfrac{1}{6}\kappa_k\int\rho_0^{5/3}dv-\tfrac{1}{3}\kappa_a\int\rho_0^{4/3}dv-\tfrac{1}{2}e^2\int\sum\frac{Z_i}{r_i}\rho_0dv-\tfrac{1}{2}V_0e\int\rho_0dv. \quad (6b)$$

As the right-hand side of Eq. (6a) shows clearly,

$$H_0<0. \quad (7)$$

To show that H_0 is a minimum, let $\rho=\rho_0+\delta\rho$, with $\delta\rho\ll\rho_0$. Then, by Eq. (1) and expanding to first powers in $\delta\rho$,

$$\begin{aligned}H(\rho_0+\delta\rho)=H_0+\int\Big[&(5/3)\kappa_k\rho_0^{2/3}+e^2\int\frac{\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}dv'-e^2\sum\frac{Z_i}{r_i}-\tfrac{4}{3}\kappa_a\rho_0^{1/3}\Big]\delta\rho dv+\int[(5/9)\kappa_k\rho_0^{-1/3}\\ &-(2/9)\kappa_a\rho_0^{-2/3}](\delta\rho)^2dv+\tfrac{1}{2}e^2\int\int\frac{\delta\rho\cdot\delta\rho'}{|\mathbf{r}-\mathbf{r}'|}dv'dv,\end{aligned}\quad (8)$$

or,

$$H(\rho_0+\delta\rho)=H_0+\sum_{j=1}^{3}I_j, \quad (8')$$

where I_j denotes the jth integral on the right in Eq. (8). Now, by (4),

$$I_1 = -V_0 e \int \delta\rho dv,$$

whence, by (3),

$$I_1 = -\delta(Ne) = 0. \tag{9a}$$

Again, from TFD theory,

$$2\kappa_k \rho_b^{-1/3} - \kappa_a \rho_b^{-2/3} = 0, \quad \rho_0 \geqslant \rho_b, \tag{9b}$$

where ρ_b is the electron density at the boundary of the TFD atom, so that

$$(5\kappa_k \rho_0^{-1/3} - 2\kappa_a \rho_0^{-2/3}) > 0, \tag{9c}$$

and hence also $I_2 > 0$. To show that also $I_3 \geqslant 0$, define the "potential" u by

$$\nabla^2 u = -4\pi\delta\rho,$$

so that

$$u = \int \frac{\delta\rho}{|\mathbf{r}-\mathbf{r}'|} dv,$$

and therefore

$$I_3 = -\frac{1}{4\pi} \int u \nabla^2 u dv;$$

but

$$\int \nabla \cdot (u \nabla u) dv = \int [u \nabla^2 u + (\nabla u)^2] dv,$$

and, upon application of Gauss' theorem to the integral on the left,

$$\int \nabla \cdot (u \nabla u) dv = \int_\infty u \nabla u \cdot d\mathbf{S} = 0,$$

whence

$$I_3 = \frac{1}{4\pi} \int (\nabla u)^2 dv \geqslant 0. \tag{9d}$$

By results (9a, c, d), the quantity added to H_0 in Eq. (8) is positive, and hence H_0 is a minimum.

B. Electric Potential and Charge Density

The electric potential is given by

$$\phi = e \sum \frac{Z_i}{r_i} - e \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} dv', \tag{10}$$

and the corresponding Poisson equation is

$$\nabla^2 \phi = -4\pi e \sum Z_i \delta(\mathbf{r}-\mathbf{r}_i) + 4\pi e \rho, \tag{11}$$

where $\delta(\mathbf{r}-\mathbf{r}_i)$ denotes the three-dimensional Dirac delta function. Thus also

$$\phi_0 = e \sum \frac{Z_i}{r_i} - e \int \frac{\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} dv', \tag{10'}$$

and

$$\nabla^2 \phi_0 = -4\pi e \sum Z_i \delta(\mathbf{r}-\mathbf{r}_i) + 4\pi e \rho_0. \tag{11'}$$

With the aid of (4), (10′) can be written

$$(5/3)\kappa_k \rho_0^{2/3} - \tfrac{4}{3}\kappa_a \rho_0^{1/3} - e(\phi_0 - V_0) = 0, \tag{12}$$

which, being a quadratic equation in $\rho_0^{1/3}$, has the solution

$$\rho_0^{1/3} = \frac{\tfrac{4}{3}\kappa_a + [(\tfrac{4}{3}\kappa_a)^2 + 4(5\kappa_k/3)(\phi_0 - V_0)e]^{1/2}}{2(5\kappa_k/3)}. \tag{13}$$

That the formal solution involving the *negative* square root in (13) is physically unacceptable can be seen from the following reasoning: Very near the nuclei, ϕ_0 can become very large, far exceeding V_0, and thus making the radical far greater than $\tfrac{4}{3}\kappa_a$; but in this case $\rho_0^{1/3}$, and hence ρ_0, would be negative, which is clearly inadmissible.

With the aid of (13), Eq. (11′) can also be written as

$$\nabla^2 \phi_0 = -4\pi e \sum Z_i \delta(\mathbf{r}-\mathbf{r}_i) + 4\pi e (2\kappa_a/5\kappa_k)^3 \times \{1 + [1 + (15\kappa_k/4\kappa_a^2) e(\phi_0 - V_0)]^{1/2}\}^3. \tag{11''}$$

Equation (11″) is the Thomas-Fermi-Dirac equation for an arbitrary number of interacting atoms.[6] Equation (13), therefore, describes the electron charge density in such a system of TFD atoms.

C. Maximization Principle

Consider the functional

$$H_1 = -\frac{1}{4\pi} \int [\tfrac{1}{2}(\nabla f)^2 + k\Psi(f) + 4\pi V_0 e \rho] dv, \tag{14}$$

where

$$f = e \sum (Z_i/r_i) - \phi, \tag{15}$$

and is subject to the boundary condition that $f \longrightarrow 0$ as $r \longrightarrow \infty$;

$$k \equiv (2^7/5^4)(\pi/3)(\kappa_a^5/\kappa_k^4) = 4\pi(5\kappa_k/3)(2\kappa_a/5\kappa_k)^5; \tag{16}$$

$$\Psi(f) \equiv \Phi(u) = \int [1 + (1+u)^{1/2}]^3 du \tag{17a}$$

$$= 4u + 2(1+u)^{3/2} + \tfrac{3}{2}u^2 + \tfrac{2}{5}(1+u)^{5/2}, \tag{17b}$$

with

$$u = b[e \sum Z_i/r_i - f - V_0] = b[\phi - V_0]; \tag{18}$$

$$b = 15\kappa_k e/4\kappa_a^2; \quad bk = 4\pi e(2\kappa_a/5\kappa_k)^3. \tag{19a,b}$$

Extremalizing H_1 by variation with respect to f, subject to the subsidiary condition (3), gives

$$\delta(H_1 + \lambda e \textstyle\int \rho dv) = 0,$$

with λ a Lagrangian multiplier to be determined below; thus,

$$-\frac{1}{4\pi} \int \left\{ \nabla f_0 \cdot \delta(\nabla f) + \left[k \frac{\partial \Phi}{\partial u} \frac{\partial u}{\partial f} + 4\pi V_0 e \frac{\partial \rho}{\partial f} - 4\pi \lambda e \frac{\partial \rho}{\partial f} \right] \delta f \right\} dv = 0. \tag{20}$$

Now

$$\int \nabla\cdot(\delta f\nabla f_0)dv=\int(\nabla f_0\cdot\nabla\delta f)dv+\int(\nabla^2 f_0)\delta f dv, \qquad (21)$$

and by application of Gauss' theorem to the integral on the left,

$$\int \nabla\cdot(\delta f\nabla f_0)dv=\int(\nabla f_0)\delta f\cdot d\mathbf{S}=0,$$

so that by (21),

$$\int(\nabla f_0\cdot\nabla\delta f)dv=-\int(\nabla^2 f_0)\delta f dv.$$

Hence, as the symbols δ and ∇ "commute", it follows from Eq. (20) that

$$-\frac{1}{4\pi}\int\Big\{-\nabla^2 f_0+k[1+(1+u_0)^{1/2}]^3(-b) +4\pi e\frac{\partial\rho}{\partial f}(V_0-\lambda)\Big\}\delta f dv=0,$$

or,

$$-\nabla^2 f_0=bk[1+(1+u_0)^{1/2}]^3+4\pi e(\partial\rho/\partial f)(\lambda-V_0). \qquad (22)$$

Also, $\nabla^2 e\sum(Z_i/r_i)=-4\pi e\sum Z_i\delta(\mathbf{r}-\mathbf{r}_i)$, so that

$$\nabla^2(e\sum Z_i/r_i-f_0)=-4\pi e\sum Z_i\delta(\mathbf{r}-\mathbf{r}_i) +bk[1+(1+u_0)^{1/2}]^3+4\pi e(\lambda-V_0)(\partial\rho/\partial f), \qquad (23)$$

which, by virtue of relations (15), (16), (18), (19) can also be expressed as

$$\nabla^2\phi_0=-4\pi e\sum Z_i\delta(\mathbf{r}-\mathbf{r}_i) +4\pi e(2\kappa_a/5\kappa_k)^3\{1+[1+(15\kappa_k/4\kappa_a^2)(\phi_0-V_0)]^{1/2}\}^3 +4\pi e(\lambda-V_0)(\partial\rho/\partial f). \qquad (24)$$

Comparison of this equation with (11″) clearly requires

$$\lambda=V_0. \qquad (25)$$

In view of this result and of (18a), Eq. (24) becomes

$$-\nabla^2 f_0=bk\{1+[1+b(e\sum Z_i/r_i-f_0-V_0)]^{1/2}\}^3. \qquad (26)$$

To show now that the extremum of H_1 is a maximum, let $f=f_0+\delta f$, with $\delta f\ll f_0$, and utilize the relations $\Psi(f_0+\delta f)=\Phi(u_0+\delta u)$, and $\rho(f_0+\delta f)=\rho_0+\delta\rho$. Then, upon expanding and retaining terms to first order in δu, one finds

$$H_1=H_{10}-\frac{1}{4\pi}\int\{\tfrac{1}{2}(\nabla\delta f)^2+\tfrac{3}{4}k[(1+u_0)^{1/4} +(1+u_0)^{-1/4}]^2(\delta u)^2\}dv-\frac{1}{4\pi}\int\{-\nabla^2 f_0 -kb[1+(1+u_0)^{1/2}]^3\}\delta f dv-\frac{1}{4\pi}V_0 e\int\delta\rho dv. \qquad (27)$$

But in view of (3) and (22), it follows that the last two integrals in (27) vanish, whereas the first integral, to be subtracted from H_{10}, is evidently positive. The extremum H_{10}, therefore, is indeed a maximum.

It will now be shown that the two extrema H_0, H_{10} are identical. We have the identity

$$\int\nabla\cdot(f_0\nabla f_0)dv=\int f_0\nabla^2 f_0 dv+\int(\nabla f_0)^2 dv,$$

and by Gauss' theorem,

$$\int\nabla\cdot(f_0\nabla f_0)dv=\int_\infty f_0\nabla f_0\cdot d\mathbf{S}=0,$$

so that

$$\int(\nabla f_0)^2=-\int f_0\nabla^2 f_0 dv,$$

and hence, by Eq. (14),

$$H_{10}=\frac{1}{8\pi}\int f_0\nabla^2 f_0 dv-\frac{1}{4\pi}\int[k\Phi(u_0)+4\pi V_0 e\rho_0]dv. \qquad (28)$$

To effect the transformation of this expression into one entirely in terms of ρ_0, we use Eqs. (12), (15), and (23), to obtain

$$\frac{1}{8\pi}\int f_0\nabla^2 f_0 dv=-\tfrac{1}{2}e^2\int\sum\frac{Z_i}{r_i}\rho_0 dv +\frac{1}{2}\int[(5/3)\kappa_k\rho_0^{5/3}-\tfrac{4}{3}\kappa_a\rho_0^{4/3}]dv+\tfrac{1}{2}V_0 e\int\rho_0 dv. \qquad (29)$$

Similarly, by Eqs. (13), (18), and (19),

$$\rho_0=(bk/4\pi e)[1+(1+u_0)^{1/2}]^3, \qquad (30)$$

and hence Eq. (17a) can be written

$$\Phi(u_0)=(4\pi e/bk)\int\rho_0(du/d\rho_0)d\rho_0. \qquad (31)$$

Using (18) and (14) to evaluate $(du/d\rho_0)$ then yields

$$\Phi(u_0)=(4\pi/k)(\tfrac{2}{3}\kappa_k\rho_0^{5/3}-\tfrac{1}{3}\kappa_a\rho_0^{4/3}), \qquad (32)$$

so that, upon substituting results (29) and (32) into Eq. (28), one has

$$H_{10}=\tfrac{1}{6}\kappa_k\int\rho_0^{5/3}dv-\tfrac{1}{3}\kappa_a\int\rho_0^{4/3}dv -\tfrac{1}{2}e^2\int\sum(Z_i/r_i)\rho_0 dv-\tfrac{1}{2}V_0 e\int\rho_0 dv, \qquad (33)$$

where the right-hand side here is identical with that of Eq. (6b), and hence

$$H_{10}=H_0. \qquad (34)$$

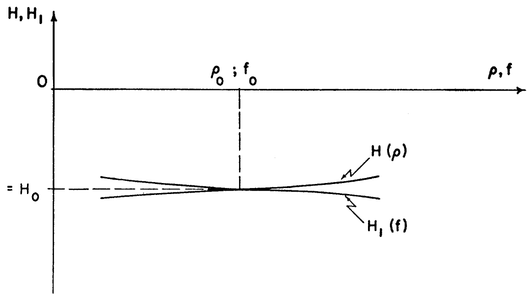

FIG. 1. Schematic representation of the (negative) functionals $H(\rho)$ and $H_1(f)$ associated, respectively, with the minimal and maximal principles.

Some of the main results concerning H and H_1 established thus far, are represented schematically in Fig. 1.

D. Significance of the Minimal and Maximal Principles

The existence of a minimization for H and of a maximization principle for H_1 is extremely useful in that it makes it possible to establish both an upper and a lower bound on H. That is, in order to calculate the exact value of $H=H_0=H_{10}$, it would be necessary to solve either the nonlinear integral equation (4) or the nonlinear differential equation (11″), which, even in the TF approximation and for only two nuclei, presents great calculational difficulties.[9]

Another approach to determine H_0 utilizes the fact, evidenced by Eqs. (8) and (9) above, that H varies slowly for small variations $\delta\rho$ about ρ_0. Thus, Lenz[13] and Jensen[14] have used $\rho=\rho_{01}+\rho_{02}$ to calculate H for two centers; and Hund,[15] using a more elaborate function, has done the same for the two special cases F_2 and N_2. Even these approximate calculations, however, are extremely tedious and require both single and double planimetry.[6] A more important deficiency in these and all similar calculations, however, is the fact that as long as the minimization principle *alone* was available, no lower bound on H was known, and hence the only accurate assertion possible was that H_0 was less than H. *How much* less, could only be guessed.[9]

With the added establishment of the maximization principle, however, this uncertainty is substantially reduced; for now another accurate assertion becomes possible, namely, that H_0 is greater than H_1. Indeed, it is readily seen from Fig. 1 that the relative error in approximating H_0 by H is

$$\epsilon\equiv(H-H_0)/|H_0|<(H-H_1)/|H|\equiv\epsilon', \quad (35a)$$

and that the mean relative error in setting $H_0\approx\frac{1}{2}(H+H_1)$ is

$$\bar{\epsilon}\equiv[\tfrac{1}{2}(H+H_1)-H_0]/|H_0|<\tfrac{1}{2}\epsilon'. \quad (35b)$$

III. THE TWO-CENTER PROBLEM IN THE TFD APPROXIMATION

A. Construction of H and H_1

Let us now employ the preceding results to obtain an upper bound on the relative error ϵ when H_0 is calculated by setting $\rho=\rho_{01}(r_1)+\rho_{02}(r_2)$ in H. Here ρ_{0i} denotes the solution of Eq. (4) for the ith atom alone.

From Eq. (4) we have

$$e^2\int\frac{\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}dv'=e^2\sum\frac{Z_i}{r_i}-(5/3)\kappa_k\rho_0{}^{2/3}+\tfrac{4}{3}\kappa_a\rho_0{}^{1/3}-V_0e, \quad (36)$$

and therefore, for the ith atom,

$$e^2\int\frac{\rho_{0i}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}dv'=e^2\frac{Z_i}{r_i}-(5/3)\kappa_k\rho_{0i}{}^{2/3}+\tfrac{4}{3}\kappa_a\rho_{0i}{}^{1/3}-V_{0i}e, \quad (37)$$

where V_{0i} denotes that part of V_0 which pertains to the ith atom.

Substituting the right-hand members of (36), (37) into Eq. (1) then gives

$$\begin{aligned}H=\kappa_k\int&[(\rho_{01}+\rho_{02})^{2/3}-\tfrac{5}{6}(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3})](\rho_{01}+\rho_{02})dv\\&-\tfrac{1}{2}e^2\int\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}\right)(\rho_{01}+\rho_{02})dv\\&-\kappa_a\int[(\rho_{01}+\rho_{02})^{1/3}-\tfrac{2}{3}(\rho_{01}{}^{1/3}+\rho_{02}{}^{1/3})](\rho_{01}+\rho_{02})dv\\&-\tfrac{1}{2}V_0e\int(\rho_{01}+\rho_{02})dv. \quad (38)\end{aligned}$$

Next, to obtain a corresponding expression for H_1, it is helpful first to transform Eq. (14) by a procedure entirely analogous to that used above in arriving at Eq. (28). This yields

$$H_1=\frac{1}{8\pi}\int f\nabla^2f\,dv-\frac{1}{4\pi}\int[k\Psi(f)+4\pi V_0e\rho]dv. \quad (39)$$

Furthermore, by (12) and (15),

$$f_0=e\sum\frac{Z_i}{r_i}-e^{-1}[(5/3)\kappa_k\rho_0{}^{2/3}-\tfrac{4}{3}\kappa_a\rho_0{}^{1/3}]-V_0, \quad (40)$$

and by (22),

$$\nabla^2f_0=-4\pi e\rho_0, \quad (41)$$

whence

$$f_{0i}=e\frac{Z_i}{r_i}-e^{-1}[(5/3)\kappa_k\rho_{0i}{}^{2/3}-\tfrac{4}{3}\kappa_a\rho_{0i}{}^{1/3}], \quad (42)$$

and

$$(1/4\pi)\nabla^2f_{0i}=-e\rho_{0i}, \quad (43)$$

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[13] W. Lenz, Z. Physik 77, 713 (1932).

[14] H. Jensen, Z. Physik 77, 722 (1932).

[15] F. Hund, Z. Physik 77, 12 (1932).

where f_{0i} denotes the solution of Eq. (26), again for the ith atom alone. Hence, if analogously to the procedure followed with regard to H, we now set $f=f_{01}(r_1)+f_{02}(r_2)$ in H_1, then Eq. (39), with the aid of Eqs. (42) and (43), gives

$$H_1=\kappa_k\int\left[\tfrac{5}{6}(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3})-\tfrac{2}{3}(\rho_{01}+\rho_{02})^{2/3}\right](\rho_{01}+\rho_{02})dv$$
$$-\kappa_a\int\left[\tfrac{2}{3}(\rho_{01}{}^{1/3}+\rho_{02}{}^{1/3})-\tfrac{1}{3}(\rho_{01}+\rho_{02})^{1/3}\right](\rho_{01}+\rho_{02})dv$$
$$-\tfrac{1}{2}e^2\int\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}\right)(\rho_{01}+\rho_{02})dv$$
$$-\tfrac{1}{2}V_0e\int(\rho_{01}+\rho_{02})dv. \quad (44)$$

With this exact form of H_1 it turned out to be impossible to obtain a numerical value for ϵ, essentially because of the complicated structural forms of H and H_1. However, using the fact that the exchange term (the term in κ_a), constitutes but a small correction[6] to the remaining terms in H_1, an expansion of $H_1(\kappa_a)$ in terms of the dimensionless parameter

$$y=\kappa_a/\left[4\kappa_ke(e\sum Z_i/r_i-f-V_0)\right]^{1/2} \quad (45)$$

was carried out to first order in κ_a, yielding

$$H_1\cong-\frac{1}{4\pi}\int\left\{\tfrac{1}{2}(\nabla f)^2+\frac{8\pi}{5}\left(\frac{3}{5\kappa_k}\right)^{3/2}\right.$$
$$\times\left[e\left(e\sum\frac{Z_i}{r_i}-f-V_0\right)\right]^{5/2}$$
$$\left.+4\pi\left(\frac{3}{5\kappa_k}\right)^2\kappa_a\left[e\sum\frac{Z_i}{r_i}-f-V_0\right]^2+4\pi eV_0\rho\right\}dv. \quad (46)$$

To perform the transformation $H_1(f)$ to $H_1(\rho_{01},\rho_{02})$, we again set $f=f_{01}(r_1)+f_{02}(r_2)$, use relations (42), (43) to introduce the electron densities ρ_{01}, ρ_{02} as before, and again expand to first order in κ_a to obtain, finally, after straightforward but lengthy algebraic manipulations,

$$H_1=\kappa_k\int\left[\tfrac{5}{6}(\rho_{01}+\rho_{02})-\tfrac{2}{3}(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3})^{3/2}\right]$$
$$\times(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3})dv-\tfrac{1}{2}e^2\int\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}\right)(\rho_{01}+\rho_{02})dv$$
$$-\kappa_a\left[\tfrac{2}{3}(\rho_{01}+\rho_{02})-\tfrac{4}{3}(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3})^{3/2}\right]$$
$$\times(\rho_{01}{}^{1/3}+\rho_{02}{}^{1/3})dv-\tfrac{1}{2}V_0e\int(\rho_{01}+\rho_{02})dv. \quad (47)$$

B. Upper Bound on the Relative Error

To facilitate now the formation of $\epsilon'\equiv(H-H_1)/|H|$, let us introduce

$$\alpha=(\rho_{01}-\rho_{02})/(\rho_{01}+\rho_{02}),\quad -1<\alpha<1. \quad (48)$$

Then we have from Eqs. (38) and (47), respectively,

$$H=\int\xi_k(\alpha)\tfrac{1}{2}\left[(5/3)\kappa_k(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3})\right](\rho_{01}+\rho_{02})dv$$
$$-\tfrac{1}{2}e^2\int\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}\right)(\rho_{01}+\rho_{02})dv$$
$$-\int\xi_a(\alpha)\tfrac{1}{2}\left[\tfrac{4}{3}\kappa_a(\rho_{01}{}^{1/3}+\rho_{02}{}^{1/3})\right](\rho_{01}+\rho_{02})dv$$
$$-\tfrac{1}{2}V_0e\int(\rho_{01}+\rho_{02})dv, \quad (49)$$

and

$$H_1=\int\eta_k(\alpha)\tfrac{1}{2}\left[(5/3)\kappa_k(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3})\right](\rho_{01}+\rho_{02})dv$$
$$-\tfrac{1}{2}e^2\int\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}\right)(\rho_{01}+\rho_{02})dv$$
$$-\int\eta_a(\alpha)\tfrac{1}{2}\left[\tfrac{4}{3}\kappa_a(\rho_{01}{}^{1/3}+\rho_{02}{}^{1/3})\right](\rho_{01}+\rho_{02})dv$$
$$-\tfrac{1}{2}V_0e\int(\rho_{01}+\rho_{02})dv, \quad (50)$$

so that

$$H-H_1=\int(\xi_k-\eta_k)\tfrac{1}{2}\left[(5/3)\kappa_k(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3})\right]$$
$$\times(\rho_{01}+\rho_{02})dv-\int(\xi_a-\eta_a)\tfrac{1}{2}\left[\tfrac{4}{3}\kappa_a(\rho_{01}{}^{1/3}+\rho_{02}{}^{1/3})\right]$$
$$\times(\rho_{01}+\rho_{02})dv, \quad (51)$$

where

$$\xi_k(\alpha)=1.2\left[\left(\frac{1+\alpha}{2}\right)^{2/3}+\left(\frac{1-\alpha}{2}\right)^{2/3}\right]^{-1}-1, \quad (52a)$$

$$\xi_a(\alpha)=1.5\left[\left(\frac{1+\alpha}{2}\right)^{1/3}+\left(\frac{1-\alpha}{2}\right)^{1/3}\right]^{-1}-1, \quad (52b)$$

$$\eta_k(\alpha)=1-0.8\left[\left(\frac{1+\alpha}{2}\right)^{2/3}+\left(\frac{1-\alpha}{2}\right)^{2/3}\right]^{3/2}, \quad (52c)$$

$$\eta_a(\alpha)=1-2\left[\left(\frac{1+\alpha}{2}\right)^{2/3}+\left(\frac{1-\alpha}{2}\right)^{2/3}\right]^{3/2}$$
$$+1.5\left\{\left[\left(\frac{1+\alpha}{2}\right)^{2/3}+\left(\frac{1-\alpha}{2}\right)^{2/3}\right]^2\Big/\right.$$
$$\left.\left[\left(\frac{1+\alpha}{2}\right)^{1/3}+\left(\frac{1-\alpha}{2}\right)^{1/3}\right]\right\}. \quad (52d)$$

Each of these four functions (52), evidently even in α, has been evaluated over the entire range of α in steps of 0.1, along with the differences $(\xi_k-\eta_k)$ and $(\xi_a-\eta_a)$, respectively, as shown in Table I.

Now from the given definitions of κ_k, κ_a, ρ_{0i}, and from the numerical values of $(\xi_k-\eta_k)\equiv\epsilon_k$, and $(\xi_a-\eta_a)\equiv\epsilon_a$, given in Table I, it follows that each of the integrals in Eq. (51) is positive, and so also is their difference, as is evident from the theory of Sec. II and Fig. 1, above.

From Eq. (51), therefore,

$$H-H_1=\int(\epsilon_kK-\epsilon_aA)dv>0, \tag{53}$$

where

$$K\equiv\tfrac{1}{2}[(5/3)\kappa_k(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3})](\rho_{01}+\rho_{02}), \tag{54a}$$

and

$$A\equiv\tfrac{1}{2}[\tfrac{4}{3}\kappa_a(\rho_{01}{}^{1/3}+\rho_{02}{}^{1/3})](\rho_{01}+\rho_{02}) \tag{54b}$$

have been introduced to simplify the notation. Similarly, let $\tilde{Z}$ and $\tilde{V}$, respectively, denote the second and fourth terms in Eq. (49). Then the latter, in view of (7), gives

$$H=\int(\xi_kK-\xi_aA)dv-(\tilde{Z}+\tilde{V})<0,$$

so that

$$|H|=(\tilde{Z}+\tilde{V})-\int(\xi_kK-\xi_aA)dv>0,$$

or

$$|H|>\tilde{Z}-\tilde{V}-\int(\xi_kK-\xi_aA)dv>0. \tag{55}$$

But by Eq. (4)

$$\tilde{Z}-\tilde{V}>\int(K-A)dv, \tag{56}$$

whence

$$|H|>\int[(1-\xi_k)K-(1-\xi_a)A]dv>0, \tag{57}$$

TABLE I. Values of ξ_k, η_k, and $(\xi_k-\eta_k)$; ξ_a, η_a, and $(\xi_a-\eta_a)$.

α	ξ_k	η_k	$\xi_k-\eta_k$	ξ_a	η_a	$\xi_a-\eta_a$
0	−0.048	−0.131	0.083	−0.055	−0.330	0.275
0.1	−0.047	−0.129	0.082	−0.053	−0.324	0.271
0.2	−0.044	−0.124	0.080	−0.050	−0.318	0.268
0.3	−0.038	−0.115	0.077	−0.044	−0.310	0.266
0.4	−0.028	−0.101	0.073	−0.035	−0.275	0.240
0.5	−0.017	−0.084	0.067	−0.025	−0.248	0.223
0.6	−0.002	−0.061	0.059	−0.008	−0.208	0.200
0.7	+0.016	−0.031	0.047	+0.017	−0.149	0.166
0.8	0.042	+0.008	0.034	0.050	−0.082	0.132
0.9	0.090	0.074	0.016	0.110	+0.034	0.076
1.0	0.200	0.200	0.000	0.500	0.500	0.000

TABLE II. Numerical values of ϵ and $\bar{\epsilon}$.

α	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
ϵ	7.91	7.84	7.66	7.42	7.10	6.59	5.90	4.78	3.58	1.80	0.00
$\bar{\epsilon}$	3.96	3.92	3.83	3.71	3.55	3.30	2.95	2.39	1.79	0.90	0.00

which, upon combination with Eq. (53), yields

$$\epsilon<\epsilon'\equiv\frac{H-H_1}{|H|}<\frac{\int(\epsilon_kK-\epsilon_aA)dv}{\int[(1-\xi_k)K-(1-\xi_a)A]dv}. \tag{58}$$

Several methods of evaluating the right-hand member of the inequality (58) exist. As an example of what is perhaps the most straightforward procedure, let us evaluate the right-hand side of (58) for the case $\alpha=0.6$, say. Then, with the aid of Table I,

$$0<(\epsilon)_{\alpha=0.6}<\frac{\int(0.059K-0.200A)dv}{\int(1.002K-1.008A)dv}$$
$$=\frac{\int[0.059(K-A)-0.141A]dv}{\int[1.002(K-A)-0.006A]dv}. \tag{59}$$

But, as is readily verified,

$$\frac{a}{b}<\frac{a+c}{b+c}, \tag{60}$$

if a, b, c are positive and $a<b$. Hence, adding $\int 0.006Adv$ to numerator and denominator in (59) gives

$$0<(\epsilon)_{\alpha=0.6}<\frac{\int[0.059(K-A)-0.135A]dv}{\int 1.002(K-A)dv}$$
$$<\frac{0.059}{1.002}\cong 5.90\%.$$

In this manner, the upper bound on ϵ and, using the simple relationship (35b), on $\bar{\epsilon}$ was evaluated, again over the entire range of α in steps of 0.1, as shown in Table II. Evidently, the maximum relative error involved in approximating H_0, the *exact* value of H on the TFD theory, by means of H of Eq. (38) is less than 7.91%; i.e.,

$$\epsilon<8\%. \tag{61}$$

Hence the mean relative error involved in approximating H_0 by $\bar{H}=\frac{1}{2}(H+H_1)$, see Eqs. (38) and (47), does not exceed 3.96%, or

$$\bar{\epsilon}<4\%. \tag{62}$$

It may be noted at this point that these values, being upper bounds, obtain only where $\alpha=0$, i.e., where $\rho_{01}\approx\rho_{02}$, but are actually smaller everywhere else.

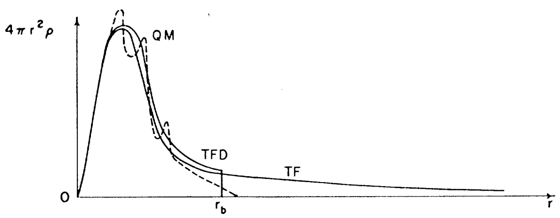

FIG. 2. Electron density distributions in TF and TFD atoms, and quantum-mechanically (Q.M.). (Schematic).

IV. THE THREE-CENTER PROBLEM IN THE TF APPROXIMATION

A. Connection to TFD Theory

The fundamental distinction between the TF and TFD models is that the latter, unlike the former, does take account of exchange effects.[6] As a consequence of this there arise the following two formal distinctions[6]: (1) The electron density ρ in the neutral TF atom extends to infinity; that in the TFD atom, to a finite boundary, defined by a radius r_b, beyond which ρ_{TFD} vanishes; see Fig. 2. (2) The Lagrangian multiplier V_0 in the TF theory vanishes for neutral atoms. Essentially all the analytic results thus far established hold, therefore, also in the TF approximation, provided we set both

$$\kappa_a=0,\quad V_0=0. \tag{63}$$

These conditions reduce the complexity of the formalism to a manageable level, and it is for this reason that the three-center problem will be treated in the simpler TF approximation.

B. Upper Bound on the Relative Error

We again wish to find an upper bound on the error ϵ_3 in calculating H_0 by using (in obvious analogy with the two center case), $\rho=\rho_{01}(r_1)+\rho_{02}(r_2)+\rho_{03}(r_3)$ and $f=f_{01}(r_1)+f_{02}(r_2)+f_{03}(r_3)$ in H and H_1, respectively, where ϵ_3 and $\bar{\epsilon}_3$ are defined as before in Eqs. (35) above.

Using (63) and introducing

$$\lambda\equiv(5/3)\kappa_k, \tag{64}$$

one then obtains in place of (38) and (47), respectively,

$$\begin{aligned}H=\lambda\int&[(5/3)(\rho_{01}+\rho_{02}+\rho_{03})^{2/3}\\&-\tfrac{1}{2}(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3}+\rho_{03}{}^{2/3})](\rho_{01}+\rho_{02}+\rho_{03})dv\\&-\tfrac{1}{2}e^2\int\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}+\frac{Z_3}{r_3}\right)(\rho_{01}+\rho_{02}+\rho_{03})dv,\end{aligned} \tag{65}$$

and

$$\begin{aligned}H_1=\lambda\int&[\tfrac{1}{2}(\rho_{01}+\rho_{02}+\rho_{03})\\&-\tfrac{2}{5}(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3}+\rho_{03}{}^{2/3})^{3/2}](\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3}+\rho_{03}{}^{2/3})dv\\&-\tfrac{1}{2}e^2\int\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}+\frac{Z_3}{r_3}\right)(\rho_{01}+\rho_{02}+\rho_{03})dv.\end{aligned} \tag{66}$$

In order to effect the numerical evaluation of the coefficient appearing in the difference between H and H_1, let us introduce the quantities β and γ defined by

$$\beta=(\rho_{01}-\rho_{02}-\rho_{03})/(\rho_{01}+\rho_{02}+\rho_{03}),\quad -1<\beta<1; \tag{67}$$

$$\gamma=(-\rho_{01}-\rho_{02}+\rho_{03})/(\rho_{01}+\rho_{02}+\rho_{03}),\quad -1<\gamma<1; \tag{68}$$

so that

$$\beta+\gamma=-2\rho_{02}/(\rho_{01}+\rho_{02}+\rho_{03})\leqslant 0, \tag{69}$$

because all $\rho_{0i}\geqslant 0$, of course.

With the aid of these quantities, Eqs. (65) and (66) can be expressed as

$$\begin{aligned}H=&\int\xi(\beta,\gamma)\tfrac{1}{2}\lambda(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3}+\rho_{03}{}^{2/3})(\rho_{01}+\rho_{02}+\rho_{03})dv\\&-\tfrac{1}{2}e^2\int\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}+\frac{Z_3}{r_3}\right)(\rho_{01}+\rho_{02}+\rho_{03})dv,\end{aligned} \tag{70}$$

$$\begin{aligned}H_1=&\int\eta(\beta,\gamma)\tfrac{1}{2}\lambda(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3}+\rho_{03}{}^{2/3})(\rho_{01}+\rho_{02}+\rho_{03})dv\\&-\tfrac{1}{2}e^2\int\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}+\frac{Z_3}{r_3}\right)(\rho_{01}+\rho_{02}+\rho_{03})dv,\end{aligned} \tag{71}$$

so that

$$\begin{aligned}H-H_1=\int&(\xi_3-\eta_3)\tfrac{1}{2}\lambda(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3}+\rho_{03}{}^{2/3})\\&\times(\rho_{01}+\rho_{02}+\rho_{03})dv,\end{aligned} \tag{72}$$

where

$$\begin{aligned}\xi_3\equiv\xi(\beta,\gamma)=1.2&\left[\left(\frac{1+\beta}{2}\right)^{2/3}+\left(\frac{1+\gamma}{2}\right)^{2/3}\right.\\&\left.+\left(\frac{\beta+\gamma}{2}\right)^{2/3}\right]^{-1}-1=\xi(\gamma,\beta),\end{aligned} \tag{73}$$

and

$$\begin{aligned}\eta_3\equiv\eta(\beta,\gamma)=1-0.8&\left[\left(\frac{1+\beta}{2}\right)^{2/3}+\left(\frac{1+\gamma}{2}\right)^{2/3}\right.\\&\left.+\left(\frac{\beta+\gamma}{2}\right)^{2/3}\right]^{3/2}=\eta(\gamma,\beta)\end{aligned} \tag{74}$$

$$=1-0.8[1.2/(1+\xi_3)]^{3/2}. \tag{74$'$}$$

The particular forms of β and γ were chosen deliberately so as to bring about the symmetries indicated in Eqs. (73) and (74), respectively. These symmetries, together with relations (69) and (74′), substantially reduce the labor involved in the computation of ξ_3 and η_3. The results of this computation over the entire range of (β,γ), in steps of 0.2 and subject to relations (69), are given in Table III, along with the corresponding differences $(\xi_3-\eta_3)$.

Two salient facts concerning $(\xi-\eta)$ are apparent from Table III: (1) $(\xi-\eta)$ is positive for all physically admissible values of (β,γ). This is in exact agreement

TABLE III. Numerical values of $\xi(\beta,\gamma)=\xi(\gamma,\beta)$; $\eta(\beta,\gamma)=\eta(\gamma,\beta)$; and $(\xi-\eta)$.

γ	−1.0	−0.8	−0.6	−0.4	−0.2	0	0.2	0.4	0.6	0.8	1.0
$\beta=-1$											
ξ	0.200	0.042	−0.002	−0.028	−0.044	−0.048	−0.044	−0.028	−0.002	0.042	0.200
η	0.200	0.008	−0.061	−0.101	−0.124	−0.132	−0.124	−0.101	−0.061	0.008	0.200
$\xi-\eta$	0.000	0.034	0.059	0.073	0.080	0.084	0.080	0.073	0.059	0.034	0.000
$\beta=-0.8$											
ξ	0.042	−0.070	−0.108	−0.126	−0.135	−0.135	−0.126	−0.108	−0.070	+0.042	···[a]
η	0.008	−0.173	−0.248	−0.287	−0.307	−0.307	−0.287	−0.248	−0.173	+0.008	···
$\xi-\eta$	0.034	0.103	0.140	0.161	0.172	0.172	0.161	0.140	0.103	0.034	···
$\beta=-0.6$											
ξ	−0.002	−0.108	−0.139	−0.154	−0.158	−0.154	−0.139	−0.107	−0.002	···	···
η	−0.061	−0.248	−0.316	−0.351	−0.361	−0.351	−0.316	−0.246	−0.061	···	···
$\xi-\eta$	0.059	0.140	0.177	0.197	0.203	0.197	0.177	0.139	0.059	···	···
$\beta=-0.4$											
ξ	−0.028	−0.126	−0.154	−0.166	−0.166	−0.154	−0.126	−0.028	···	···	···
η	−0.101	−0.287	−0.351	−0.381	−0.381	−0.351	−0.287	−0.101	···	···	···
$\xi-\eta$	0.073	0.161	0.197	0.215	0.215	0.197	0.161	0.073	···	···	···
$\beta=-0.2$											
ξ	−0.044	−0.135	−0.158	−0.166	−0.158	−0.135	−0.044	···	···	···	···
η	−0.124	−0.307	−0.361	−0.381	−0.361	−0.307	−0.124	···	···	···	···
$\xi-\eta$	0.080	0.172	0.203	0.215	0.203	0.172	0.080	···	···	···	···
$\beta=0$											
ξ	−0.048	−0.135	−0.154	−0.154	−0.135	−0.048	···	···	···	···	···
η	−0.132	−0.307	−0.351	−0.351	−0.307	−0.132	···	···	···	···	···
$\xi-\eta$	0.084	0.172	0.197	0.197	0.172	0.084	···	···	···	···	···
$\beta=+0.2$											
ξ	−0.044	−0.126	−0.139	−0.126	−0.044	···	···	···	···	···	···
η	−0.124	−0.287	−0.316	−0.287	−0.124	···	···	···	···	···	···
$\xi-\eta$	0.080	0.161	0.177	0.161	0.080	···	···	···	···	···	···
$\beta=0.4$											
ξ	−0.028	−0.108	−0.108	−0.028	···	···	···	···	···	···	···
η	−0.101	−0.248	−0.248	−0.101	···	···	···	···	···	···	···
$\xi-\eta$	0.073	0.140	0.140	0.073	···	···	···	···	···	···	···
$\beta=0.6$											
ξ	−0.002	−0.070	−0.002	···	···	···	···	···	···	···	···
η	−0.061	−0.173	−0.061	···	···	···	···	···	···	···	···
$\xi-\eta$	0.059	0.103	0.059	···	···	···	···	···	···	···	···
$\beta=0.8$											
ξ	0.042	0.042	···	···	···	···	···	···	···	···	···
η	0.008	0.008	···	···	···	···	···	···	···	···	···
$\xi-\eta$	0.034	0.034	···	···	···	···	···	···	···	···	···
$\beta=1.0$											
ξ	0.200	···	···	···	···	···	···	···	···	···	···
η	0.200	···	···	···	···	···	···	···	···	···	···
$\xi-\eta$	0.000	···	···	···	···	···	···	···	···	···	···

[a] All spaces marked ··· only correspond to sets (β,γ) which, by relation (69), are physically inadmissible.

with the requirement that, by the theory concerning the minimal and maximal principles of Sec. II above, the quantity $(H-H_1)$ in Eq. (72) must be positive. (See also Fig. 1.) Hence, as λ and the ρ_{0i} on the right-hand side of (72) are all essentially positive, so must $(\xi-\eta)$ be. (2) The maximum value of $(\xi-\eta)$, somewhat greater than 0.215, seems to occur somewhere between the points $(\beta,\gamma)=(-0.4,\ -0.4)$ and $(-0.4,\ -0.2)$ or $(-0.2,\ -0.4)$. This, too, is found to be in close agreement with the value of

$$(\xi-\eta)_{\max}=0.2176 \quad \text{at} \quad \beta=\gamma=-\tfrac{1}{3}, \tag{75}$$

obtained analytically.

By virtue of (75), Eq. (72) gives

$$(H-H_1)<0.218\int\lambda\tfrac{1}{2}(\rho_{01}{}^{2/3}+\rho_{02}{}^{2/3}+\rho_{03}{}^{2/3}) \times(\rho_{01}+\rho_{02}+\rho_{03})dv. \tag{76}$$

From Eq. (4) we have, using also relations (63) and (64) appropriate for the TF case,

$$\lambda\rho_{0i}{}^{2/3}<e^2(Z_i/r_i), \tag{77}$$

so that

$$(H-H_1)<0.218\int\tfrac{1}{2}e^2\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}+\frac{Z_3}{r_3}\right) \times(\rho_{01}+\rho_{02}+\rho_{03})dv. \tag{78}$$

Also, as $H<0$, it follows from (70) and (77) that

$$|H|>\tfrac{1}{2}e^2\int(1-\xi_3)\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}+\frac{Z_3}{r_3}\right)\times(\rho_{01}+\rho_{02}+\rho_{03})dv. \quad (79)$$

The lower bound on $|H|$ is clearly obtained with $\xi=\xi_{\max}$, which latter is found from Table III to be

$$\xi_{\max}=0.200, \quad (80)$$

so that

$$|H|>0.800\int\tfrac{1}{2}e^2\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}+\frac{Z_3}{r_3}\right)(\rho_{01}+\rho_{02}+\rho_{03})dv, \quad (81)$$

whence, upon combining this result with (78), one finally obtains the desired values:

$$\epsilon_3<(0.218/0.800)\simeq 27\%, \quad (82a)$$

and

$$\bar{\epsilon}_3\lesssim 13.5\%. \quad (82b)$$

The mean $\frac{1}{2}(H+H_1)$ thus differs from H_0, the exact value (in the TF approximation), by not more than $\sim$13.5%, an error well within the over-all accuracy of 20% of the TF model.[16] It may further be noted that, in general, the error ϵ_3 (or $\bar{\epsilon}_3$) will be very much less than the upper bound(s) calculated here. This is so because the values of ϵ_3 and $\bar{\epsilon}_3$ depend, through Eqs. (78) and (79), essentially on the ratio $(\xi-\eta)/(1-\xi)$, which latter generally is very much smaller than $(\xi-\eta)_{\max}/(1-\xi_{\max})$. Thus, at $(\beta,\gamma)=(-0.2,-0.8)$ for example, one finds, using Table III,

$$\epsilon_3<(0.172/1.135)\simeq 15\%, \quad (83a)$$

so that

$$\bar{\epsilon}_3<7.5\%. \quad (83b)$$

V. THE INTERACTION POTENTIALS

A. The TFD Two-Center System

Defining the interaction potential $U(R)$ as the sum of the Coulomb interaction between the atomic nuclei and the change in the electron energies brought about by the approach of the nuclei to a mutual distance R, we have for a two-center system,

$$U(R)=Z_1Z_2e^2/R+H-H(\infty), \quad (84)$$

$$U_1(R)=Z_1Z_2e^2/R+H_1-H_1(\infty), \quad (85)$$

where Z_1, Z_2 denote the atomic numbers of atoms 1 and 2, respectively. More explicitly, with the aid of Eqs. (38) and (44),

$$\begin{aligned}U(R)=Z_1Z_2e^2/R&\\ &+\int\Big\{\kappa_k\big[(\rho_{01}+\rho_{02})^{5/3}-\tfrac{5}{6}(\rho_{01}^{2/3}+\rho_{02}^{2/3})\\ &\times(\rho_{01}+\rho_{02})-\tfrac{1}{6}(\rho_{01}^{5/3}+\rho_{02}^{5/3})\big]\\ &-\kappa_a\big[(\rho_{01}+\rho_{02})^{4/3}-\tfrac{2}{3}(\rho_{01}^{1/3}+\rho_{02}^{1/3})\\ &\times(\rho_{01}+\rho_{02})-\tfrac{1}{3}(\rho_{01}^{4/3}+\rho_{02}^{4/3})\big]\\ &-\tfrac{1}{2}e^2\left(\frac{Z_1}{r_1}\rho_{02}+\frac{Z_2}{r_2}\rho_{01}\right)\Big\}dv, \quad (86)\end{aligned}$$

$$\begin{aligned}U_1(R)=Z_1Z_2e^2/R&\\ &+\int\Big\{\kappa_k\big[\tfrac{5}{6}(\rho_{01}^{2/3}+\rho_{02}^{2/3})(\rho_{01}+\rho_{02})\\ &-\tfrac{2}{3}(\rho_{01}+\rho_{02})^{5/3}-\tfrac{1}{6}(\rho_{01}^{5/3}+\rho_{02}^{5/3})\big]\\ &-\kappa_a\big[\tfrac{2}{3}(\rho_{01}^{1/3}+\rho_{02}^{1/3})(\rho_{01}+\rho_{02})\\ &-\tfrac{1}{3}(\rho_{01}+\rho_{02})^{4/3}-\tfrac{1}{3}(\rho_{01}^{4/3}+\rho_{02}^{4/3})\big]\\ &-\tfrac{1}{2}e^2\left(\frac{Z_1}{r_1}\rho_{02}+\frac{Z_2}{r_2}\rho_{01}\right)\Big\}dv. \quad (87)\end{aligned}$$

Recalling now that

$$H_1<H_0<H<0, \quad (88)$$

it is clear that

$$U_1<U_0<0, \quad (89)$$

where U_0 is the exact repulsive interaction potential. Hence, if for brevity we set $\bar{Z}\equiv Z_1Z_2e^2/R$, then

$$\begin{aligned}\frac{U-U_0}{U_0}<\frac{U-U_1}{U_1}&\\ &=\frac{\bar{Z}+H-H(\infty)-[\bar{Z}+H_1-H(\infty)]}{\bar{Z}+H_1-H_1(\infty)}\\ &=\frac{H-H_1-[H(\infty)-H_1(\infty)]}{|Z|+|H_1(\infty)|-|H_1|}<\frac{H-H_1}{|H|}\equiv\epsilon' \quad (90)\end{aligned}$$

whence it follows, in view of result (62), that the mean relative error, not only in the total electron energy $\bar{H}\equiv\frac{1}{2}(H+H_1)$, but also in the interaction energy $\bar{U}=\frac{1}{2}(U+U_1)$ is not greater than $\sim$4%:

$$\bar{\epsilon}_U<4\%. \quad (91)$$

That is, the mean relative error in calculating U_0 by using $\frac{1}{2}(U+U_1)$ as obtainable from Eqs. (86) and (87) will be less than 4%; or, if U alone be used, the relative error will be less than 8%.

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[16] O. B. Firsov, J. Exptl. Theoret. Phys. U.S.S.R. **33**, 696 (1957) [translation: Soviet Phys.—JETP **6**(33), 534 (1958)].

Introduction of the TFD *Screening Function*

For the twofold purpose of achieving greater conciseness and aiding in the numerical computation of $U(R)$, it is desirable to simplify the two results (86) and (87) as follows: Let $\bar{K}$ and $\bar{A}$ denote the integrals in (86) involving κ_k and κ_a, respectively. Then (86) can be written as

$$U(R)=\tfrac{1}{2}Z_1e\left[\frac{Z_2e}{R}-e\int\frac{\rho_{02}}{r_1}dv\right]+\tfrac{1}{2}Z_2e\left[\frac{Z_1e}{R}-e\int\frac{\rho_{01}}{r_2}dv\right]+\bar{K}-\bar{A}. \tag{92}$$

But the expression contained in the first square brackets above is just the TFD potential ϕ_2 due to atom 2 at a distance R from it, and similarly, the expression in the second set of brackets represents the TFD potential ϕ_1 due to atom 1 at a distance R from it.

Also, from TFD theory,[6]

$$\phi(R)=(Ze/R)\psi(x)-\kappa_a^2/(60\kappa_ke),\quad x\leqslant x_b, \tag{93}$$

where

$$x=R/\mu, \tag{94}$$

$$\mu=\tfrac{1}{4}(9\pi^2/2Z)^{1/3}a_0=0.8853a_0/Z^{1/3}, \tag{95}$$

and $\psi(x)$ is the TFD screening function. Hence, if we introduce the further abbreviations

$$\Lambda\equiv\bar{K}-\bar{A},\quad\text{and}\quad a\equiv0.8853a_0=0.468\times10^{-8}\text{ cm}, \tag{96,97}$$

then Eq. (92) becomes

$$U(R)=(\tfrac{1}{2}Z_1Z_2e^2/R)[\psi(Z_1^{1/3}R/a)+\psi(Z_2^{1/3}R/a)]-(\kappa_a^2/120\kappa_k)(Z_1+Z_2)+\Lambda, \tag{98}$$

and in precisely the same manner,

$$U_1(R)=(\tfrac{1}{2}Z_1Z_2e^2/R)[\psi(Z_1^{1/3}R/a)+\psi(Z_2^{1/3}R/a)]-(\kappa_a^2/120\kappa_k)(Z_1+Z_2)+\Lambda_1, \tag{99}$$

where

$$\Lambda_1\equiv\bar{K}_1-\bar{A}_1, \tag{100}$$

and $\bar{K}_1$ and $\bar{A}_1$, respectively, denote the integrals involving κ_k, κ_a in (87). Finally, setting

$$\bar{\Lambda}\equiv\tfrac{1}{2}(\Lambda+\Lambda_1), \tag{101}$$

one finds, in view of (91), that

$$\bar{U}(R)=(\tfrac{1}{2}Z_1Z_2e^2/R)[\psi(Z_1^{1/3}R/a)+\psi(Z_2^{1/3}R/a)]-(\kappa_a^2/120\kappa_k)(Z_1+Z_2)+\bar{\Lambda}, \tag{102}$$

when used to calculate $U_0(R)$, will involve a mean relative error of less than 4% (in the TFD approximation). Equations (91) and (102) are the central results of this paper with regard to a TFD two-center system.

B. The TF Three-Center System

We restrict our considerations here to a system of three atoms, the nuclei of which occupy the vertices of an equilateral triangle of side R. Then, by generalizing the definitions (84), (85), we have here

$$U(R)=\sum_{\substack{i,j=1\\i<j}}^{3}{}'\,(Z_iZ_je^2/R)+H-H(\infty), \tag{103}$$

and

$$U_1(R)=\sum_{\substack{i,j=1\\i<j}}^{3}{}'\,(Z_iZ_je^2/R)+H_1-H_1(\infty), \tag{104}$$

where the primes on the summation signs indicate that the terms in $i=j$ are to be excluded. Hence, with the aid of Eqs. (65), (66), one obtains

$$\begin{aligned}U(R)=(e^2/R)\sum_{\substack{i,j=1\\i<j}}^{3}{}'\,Z_iZ_j&+\lambda\int\Big[\tfrac{3}{5}\Big(\sum_{m=1}^{3}\rho_{0m}\Big)^{5/3}-\tfrac{1}{2}\Big(\sum_{m=1}^{3}\rho_{0m}^{2/3}\Big)\Big(\sum_{m=1}^{3}\rho_{0m}\Big)\\&-\tfrac{1}{10}\sum_{m=1}^{3}\rho_{0m}^{5/3}\Big]dv-\tfrac{1}{2}e^2\int\Big[\frac{Z_1}{r_1}(\rho_{02}+\rho_{03})\\&+\frac{Z_2}{r_2}(\rho_{03}+\rho_{01})+\frac{Z_3}{r_3}(\rho_{01}+\rho_{02})\Big]dv.\end{aligned} \tag{105}$$

$$\begin{aligned}U_1(R)=(e^2/R)\sum_{\substack{i,j=1\\i<j}}^{3}{}'\,Z_iZ_j&+\lambda\int\Big[\tfrac{1}{2}\Big(\sum_{m=1}^{3}\rho_{0m}\Big)\Big(\sum_{m=1}^{3}\rho_{0m}^{2/3}\Big)-\tfrac{2}{5}\Big(\sum_{m=1}^{3}\rho_{0m}^{2/3}\Big)^{5/2}\\&-\tfrac{1}{10}\sum_{m=1}^{3}\rho_{0m}^{5/3}\Big]dv-\tfrac{1}{2}e^2\int\Big[\frac{Z_1}{r_1}(\rho_{02}+\rho_{03})\\&+\frac{Z_2}{r_2}(\rho_{03}+\rho_{01})+\frac{Z_3}{r_3}(\rho_{01}+\rho_{02})\Big]dv.\end{aligned} \tag{106}$$

Since the terms in Z_iZ_j vanish upon formation of the difference $(U-U_1)$, it follows by reasoning exactly analogous to that leading to relation (90) above, that here, too, $(U-U_0)/U_0<(H-H_1)/|H|\equiv\epsilon_3'$, whence, using (82),

$$\bar{\epsilon}_3<13.5\%. \tag{107}$$

That is, by results (82) of Sec. IV, the mean relative error in calculating the interaction energy U_0 by using $\frac{1}{2}(U+U_1)$ as obtainable from Eqs. (103) and (104), is less than 13.5%; or if H alone be used, the relative error will not exceed 27%.

Introduction of the TF *Screening Function*

Let Λ_3' and Λ_{31}' denote the terms involving λ in Eqs. (105) and (106), respectively. (The primes on the symbols Λ will distinguish quantities in TF theory from corresponding ones in the TFD theory.) Then, upon rearranging the terms involving the Z_i, these Eqs. can be written as

$$\begin{aligned}U(R)=\tfrac{1}{2}Z_1e^2\left(\frac{Z_2}{R}-\int\frac{\rho_{02}}{r_1}dv\right)+\tfrac{1}{2}Z_2e^2\left(\frac{Z_1}{R}-\int\frac{\rho_{01}}{r_2}dv\right)\\ +\tfrac{1}{2}Z_2e^2\left(\frac{Z_3}{R}-\int\frac{\rho_{03}}{r_2}dv\right)+\tfrac{1}{2}Z_3e^2\left(\frac{Z_2}{R}-\int\frac{\rho_{02}}{r_3}dv\right)\\ +\tfrac{1}{2}Z_3e^2\left(\frac{Z_1}{R}-\int\frac{\rho_{01}}{r_3}dv\right)+\tfrac{1}{2}Z_1e^2\left(\frac{Z_3}{R}-\int\frac{\rho_{03}}{r_1}dv\right)\\ +\Lambda_3',\end{aligned}\qquad(108)$$

$$U_1(R)=\bar{Z}'+\Lambda_{31}',\qquad(109)$$

where $\bar{Z}'$ denotes the right-hand member of (108) exclusive of Λ_3'. But

$$e\left(\frac{Z_i}{R}-\int\frac{\rho_{0i}}{r_j}dv\right)=\left\{\begin{matrix}\text{TF potential due to atom } i\\ \text{at a distance } R \text{ from it;}\end{matrix}\right\},$$

where i, $j=1$, 2, 3; $i\neq j$; and from TF theory,[6]

$$\phi(R)=(Ze/R)\chi(x),\qquad(110)$$

where x is the same as defined by (94) above, and $\chi(x)$ is the TF screening function. Thus (108), (109) may be written

$$U(R)=\mathrm{X}+\Lambda_3',\qquad(111)$$

$$U_1(R)=\mathrm{X}+\Lambda_{31}',\qquad(112)$$

where

$$\mathrm{X}\equiv(\tfrac{1}{2}e^2/R)\{\sum_{\substack{i,\,j=1\\ i<j}}^{3}{}' Z_iZ_j[\chi(x_i)+\chi(x_j)]\}.\qquad(113)$$

Setting

$$\bar{\Lambda}_3'\equiv\tfrac{1}{2}(\Lambda_3'+\Lambda_{31}'),\qquad(114)$$

one finds

$$\bar{U}(R)=\mathrm{X}+\bar{\Lambda}_3',\qquad(115)$$

which, when employed in calculating the interaction energy U_0 by using $\frac{1}{2}(U+U_1)$, will involve a mean relative error of less than 13.5%; or, if U alone be used, a relative error of less than 27%. Equations (107) and (115) are the main results of this paper with regard to a TF three-center system.

C. The TF Two-Center System

It may be observed that Eqs. (111), (112) correctly reduce to the TF two-center interaction potentials given by Firsov.[16] For if we set, say, $Z_3=0$, $\rho_{03}=0$, then two of the terms in (113) vanish, thus reducing (111) and (112), respectively, to

$$U(R)=\tfrac{1}{2}(Z_1Z_2e^2/R)[\chi(x_1)+\chi(x_2)]+\Lambda',\qquad(116)$$

and

$$U_1(R)=\tfrac{1}{2}(Z_1Z_2e^2/R)[\chi(x_1)+\chi(x_2)]+\Lambda_1'.\qquad(117)$$

These are evidently the exact TF analogs of our TFD results (98) and (99), respectively.

VI. DISCUSSION

A. Range of Validity of the Potentials

The domain of applicability of both our central results, Eq. (102) for the TFD two-center system and Eq. (115) for the TF three-center system, is restricted in the following manner. Recalling that the TFD atom is confined entirely within a sphere of radius r_b, different for each atomic species (see Fig. 2), it is clear that for $R>(r_{b1}+r_{b2})$, the actual interaction energy of the undistorted, nonoverlapping atoms 1 and 2 must vanish. Yet our formula (102) for $\bar{U}_{\mathrm{TFD}}$ does not appear to guarantee such vanishing, and moreover will contain

$$\psi(x)=\frac{R}{Ze}\frac{\kappa_a{}^2}{60\kappa_k e}=\left\{\begin{matrix}\text{constant for}\\ \text{a given } Z\end{matrix}\right\}\quad\text{when}\quad x>x_b,\qquad(118)$$

[see Eq. (93)]. We, therefore, conclude that $\bar{U}_{\mathrm{TFD}}$ may become inaccurate when R exceeds r_{b1} or r_{b2}, whichever is the smaller, and that $\bar{U}_{\mathrm{TFD}}$ becomes inapplicable when R exceeds $(r_{b1}+r_{b2})$.

The TF electron distribution involved in formula (115), on the other hand, vanishes too slowly as $r\rightarrow\infty$ (see Fig. 2),[6] and the TF screening function χ is considered[16] acceptable only out to $r\sim1$ A, or $\sim2\,a_0$. Hence, result (115) for $\bar{U}_{\mathrm{TF}}$ may become unreliable when the internuclear distance R exceeds ~1 A or $\sim2\,a_0$.

B. Applications

Preliminary calculations using the TFD two-center interaction potential $\bar{U}(R)$ of Eq. (102) for such systems as A-A; Ne-Ne; Kr-Kr; but also for some non-spherically symmetric atoms, and hetero-nuclear systems have been made. All these tend to indicate that: (1) For very small separations of less than $\sim0.3\,a_0$, $\bar{U}$ agrees well with other theoretical curves and with experiment. (2) In the intermediate range from $\sim0.3\,a_0$ to $\sim3\,a_0$, $\bar{U}$ agrees better with other theoretical curves and experimental curves than does Bohr's screened

Coulomb potential[17] or that based on the TF approximation.[16] It is expected that the results of these calculations will be reported in detail in a later paper.

On the basis of these results, it may then be of interest to calculate atomic scattering cross sections (in suitable energy intervals), and to perform range-energy calculations, both capable of being verified by experiment.[18–20] Furthermore, the TF three-center potential (115) may be applied to suitable triatoms. Lastly, a generalization of the formalism developed in this paper to *ionic* systems would evidently still further enhance its usefulness.

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Onset of Correlation in Initially Uncorrelated System

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The system under consideration is a number of molecules contained in a resonant cavity and isolated from external influences. The molecules are assumed to have two energy levels, and the molecular frequencies have a Gaussian distribution centered at the cavity frequency; the initial states of the molecules are uncorrelated. The onset of correlation in the molecular behavior is studied by examining the field in the cavity and the power emitted by the molecules for effects depending on the square of the number of molecules, in a perturbation theory approach.

It is shown that correlation effects manifest themselves in the fourth order interaction. Both the correlation energy in the field and the correlation power emitted by the molecules approach steady-state values after transient periods determined by the relaxation time of the cavity and the frequency spread of the molecules. A physical picture of the correlation effects, as being due to induced emission produced by the lowest order spontaneous and thermal emission, is investigated and found to be approximately correct. The ratio of correlation energy to lowest order spontaneous emission energy is derived. An analysis is made of the dependence of the results on the initial states of the molecules, and interpreted in terms of the physical picture. The effect of the presence of a number of cavity modes, rather than a single mode, within the frequency spread of the molecules is investigated under simplifying assumption, and is shown to multiply the correlation effects by the square of the number of modes.

INTRODUCTION

THE subject of correlation in a many-body system includes a large number of diverse problems, some of which have become very popular recently. Correlation is caused, of course, by a coupling between the individual bodies of the system, which can take one one or more of several forms. The problem to be treated in the present article deals with the correlation of a number of atomic systems, which we refer to as molecules, coupled to one another through the electromagnetic field in a resonant cavity. The question we ask is the following: Suppose we have a cavity containing a number of molecules that are isolated from external influences and are initially in uncorrelated states. Will correlation arise, and if so, in what manner?

The meaning of correlation in the present context will be described first. The molecules are uncorrelated if the state of each molecule is independent of the other molecules. Correlation may be measured by the extent to which the behavior of each molecule is affected by the others. The difference between the behavior of molecules in correlated and uncorrelated states has been discussed in some detail by both Dicke[1] and the author.[2] In reference 2 it is shown that when molecules are in a correlated state, spontaneous emission is proportional to N^2, where N is the number of molecules; if the molecules are in an uncorrelated state that is also an energy state, spontaneous emission is proportional to N. There are, however, uncorrelated states in which each molecule is in the same superposition of individual energy states, and in this case the spontaneous emission is also proportional to N^2. The latter type of state may be regarded as corresponding to a classical array of dipoles oscillating with the same well-defined phase; it can be created by subjecting the molecules to an external driving field. We are excluding the consideration of such classical-type correlations, since they cannot arise in an isolated system, and use the term correlation to indicate only quantum-mechanical correlation. (In the language of reference 2, the case in which each molecule is in the same superposition of individual energy states is called uncorrelated but coherent.) Incidentally, as explained in reference 2, in the correlated energy state the molecules may also be regarded as oscillating in phase with each other, but the absolute phase is completely undetermined.[3] With

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[3] We give a simple illustration of correlated and uncorrelated states for the case of two similar molecules. If φ_{mi} is the i'th energy state of the mth molecule, then $\varphi_{1i}\varphi_{2j}$ is an uncorrelated energy state, and $2^{-\frac{1}{2}}(\varphi_{1i}\varphi_{2j}\pm\varphi_{1j}\varphi_{2i})$ is a correlated energy state. In the language of reference 2, $\psi_1\psi_2$, where $\psi_m=a_1\varphi_{m1}+a_2\varphi_{m2}$, is a coherent uncorrelated state.