PHYSICAL REVIEW A VOLUME 34, NUMBER 1 JULY 1986

Universal nature of van der Waals forces for Coulomb systems

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(Received 2 December 1985)

The nonrelativistic Schrödinger equation is supposed to yield a pairwise R^{-6} attractive interaction among atoms or molecules for large separation, R. Up to now this attraction has been investigated only in perturbation theory or else by invoking various assumptions and approximations. We show rigorously that the attraction is at least as strong as R^{-6} for any shapes of the molecules, independent of other features such as statistics or sign of charge of the particles. More precisely, we prove that two neutral molecules can always be oriented such that the ground-state energy of the combined system is less than the sum of the ground-state energies of the isolated molecules by a term $-cR^{-6}$ provided R is larger than the sum of the diameters of the molecules. When several molecules are present, a pairwise bound of this kind is derived. In short, we prove that in the quantum mechanics of Coulomb systems everything binds to everything else if the nuclear motion is neglected.

I. INTRODUCTION

Our purpose is to explore and to answer some elementary but fundamental questions about the binding of neutral atoms and molecules. To simplify matters, we shall use the infinite nuclear-mass approximation in which the nuclei are held fixed, but many of our mathematical constructions can, with additional work and appropriate changes, be carried over to the more realistic case of dynamic nuclei. In our fixed-nuclei approximation we do *not* assume that the nuclei are necessarily in the configuration that minimizes the energy of the molecule.

Consider two neutral molecules (or atoms) labeled α and β, with respective diameters $2r^\alpha$ and $2r^\beta$, and whose centers are separated by a distance $R^{\alpha\beta} > r^\alpha + r^\beta$. (The precise definition of r^α, r^β, and $R^{\alpha\beta}$ will be given in Sec. III.) Let the ground-state energies of the isolated molecules and of the combined system be e^α, e^β, and $e(R^{\alpha\beta})$, respectively. The question we shall address is this: Is it possible to orient the nuclear coordinates at the two neutral molecules with respect to each other (with $R^{\alpha\beta}$ fixed) so that after an appropriate readjustment of the electronic wave function

$$e(R^{\alpha\beta}) < e^\alpha + e^\beta \, ? \tag{1.1}$$

In particular, is there an upper bound of the van der Waals form

$$e(R^{\alpha\beta}) \le e^\alpha + e^\beta - C(R^{\alpha\beta})^{-6} \tag{1.2}$$

for a constant $C > 0$ which depends on the intrinsic properties of the two molecules, but not on $R^{\alpha\beta}$?

We shall prove, using a variational argument, that Eq. (1.2) is true; in other words, we prove that "everything binds to everything else" when the nuclear kinetic energy is neglected. First, several remarks are in order.

(1) Equation (1.2), or even Eq. (1.1), implies binding in the fixed-nuclei approximation. When the nuclear kinetic energy is added, the uncertainty principle may destroy the binding, as is probably the case for He_2. Thus we can only say that sufficiently heavy isotopes will always bind.

(2) Density-functional theories (at least the ones known to us) fail to predict Eq. (1.2). Although a density functional that predicts Eq. (1.2) exists in principle,[1,2] no one has actually constructed one. In Thomas-Fermi theory even Eq. (1.1) fails because Teller's theorem[3] states that in Thomas-Fermi theory $e(R^{\alpha\beta}) > e^\alpha + e^\beta$ always. When gradient corrections are added, as in Thomas—Fermi—von Weizsäcker theory, Eq. (1.1) holds[3] when $R^{\alpha\beta} \approx r^\alpha + r^\beta$ but Eq. (1.2) fails when $R^{\alpha\beta} \gg r^\alpha + r^\beta$. The reason for this failure of (local) density-functional theory (as explained in Refs. 2 and 3) is the following.

The R^{-6} attraction comes from a dipole-dipole interaction but (in the combined system) there is almost no static dipole moment in each molecule (if both molecules were free of static dipole moments in their ground states). The interaction energy of dipole moments $\mathbf{d}^\alpha$ and $\mathbf{d}^\beta$ on the respective molecules is proportional to $-d^\alpha d^\beta (R^{\alpha\beta})^{-3}$. Density-functional theory, since it deals only with single-particle densities, can produce these only as static moments and at an energy cost of $\frac{1}{2}c^\alpha (d^\alpha)^2 + \frac{1}{2}c^\beta (d^\beta)^2$. Thus, when $R^{\alpha\beta} > (c^\alpha c^\beta)^{1/6}$ the optimum choice is $d^\alpha = d^\beta = 0$ and there is no attraction.

The true source of the R^{-6} term in Eq. (1.2) is a correlation effect between the electrons in molecule α and those in molecule β. It is essential to think of electrons as particles and not as a simple fluid. In the language of quantum mechanics the molecules make a virtual transition (simultaneously and not separately) to an excited state. The energy to create d^α and d^β is then (from second-order perturbation theory) proportional to $(d^\alpha d^\beta)^2$. The minimum with respect to d^α and d^β for fixed $R^{\alpha\beta}$ of

$(d^\alpha d^\beta)^2 - d^\alpha d^\beta (R^{\alpha\beta})^{-3}$ is the required $-(R^{\alpha\beta})^{-6}$. Apart from the fact that quantum mechanics is needed in order to give meaning to the concept of the ground state, the effect is classical insofar as no interference effect is involved. There is simply a coherence in the motion of the electrons in each molecule so that the (time) average dipole-dipole interaction is not zero even though the average dipole moment of each molecule is essentially zero.

(3) When one studies the question of the additivity of the van der Waals forces between pairs of molecules the correlation effect appears even more strikingly. The Coulomb interaction correlates the dipole moments $\mathbf{d}^\alpha$ and $\mathbf{d}^\beta$ with the displacement $\mathbf{R}^{\alpha\beta}$ between them in such a way as to give the directional factor $-3(\mathbf{d}^\alpha \cdot \mathbf{R}^{\alpha\beta})(\mathbf{d}^\beta \cdot \mathbf{R}^{\alpha\beta}) + (\mathbf{d}^\alpha \cdot \mathbf{d}^\beta) \, | \mathbf{R}^{\alpha\beta} |^2$ as function of direction its minimal value, $-2 | \mathbf{d}^\alpha | \; | \mathbf{d}^\beta | \; | \mathbf{R}^{\alpha\beta} |^2$, *simultaneously* for all pairs. Thus the nonstatic dipole moments $\mathbf{d}^\alpha$ do not depend on the *single* molecules, but only on the *pairs* of molecules which interact with each other. As a consequence, our bounds on the effective interaction potentials will add together like scalar potentials and not like dipole potentials. This does not, of course, imply that the true effective interaction potential has this property.

(4) The analysis in remark (2) was based on the Coulomb potential, but presumably this is not essential. If the electron-electron interaction were r^{-p} instead of r^{-1}, we should expect the appropriate modification of Eq. (1.2) would have R^{-2p-4} in place of R^{-6}. We shall not pursue this aspect of the problem, however, and will confine our attention to the Coulomb potential.

(5) It is not at all essential that the dynamic particles are electrons. They could be any mixture of bosons and fermions. Also, for example, matter and antimatter will bind in the infinite nuclear-mass approximation—which carries the physical implication that there is no quantum-mechanical Coulomb barrier to the annihilation process. There are several variational calculations of the dependence of the energy on the nuclear separation, but with different conclusions.[4–6]

(6) No assumption is made about the spherical symmetry of the two molecules and they could have permanent electric dipole or higher-pole moments in their ground states (but not monopole moments). Parity conservation does not preclude this since the nuclear coordinates are fixed. A feature of Eq. (1.2) is that it is independent of any assumption about the permanent moments; if any exist then the binding could be stronger, but not weaker than R^{-6}.

(7) There is, of course, an enormous amount of literature about van der Waals forces (see, e.g., Refs. 7—9). In a certain sense our results are thus not new, but from another point of view they are new. The drawback to the usual theories is that they are always based on perturbation theory in two ways: (i) One assumes that R is sufficiently large so that the $1/r$ Coulomb interaction can be expanded up to the dipole-dipole order, and all higher terms ignored. Although it can be shown that this expansion is asymptotically exact,[10] we are usually not told how large this R has to be. (ii) One uses second-order quantum perturbation theory—and this is usually calculated with some unverified assumptions about the excited-state molecular or atomic wave functions. Our point is that none of this is necessary. While we make no pretense to getting the correct constant C in Eq. (1.2), we do get a lower bound to the binding energy of the correct form (when $R > r^\alpha + r^\beta$) by a fairly simple and direct variational argument.

(8) Another point about the standard theory that needs to be addressed is the well-known effect of retardation discovered by Casimir and Polder[11] and elaborated by Lifshitz.[12] The R^{-6} term in Eq. (1.2) is replaced by R^{-7} when R is "large." However, large means (Bohr radius)/(fine-structure constant) and this is huge compared to $r^\alpha + r^\beta$ (for molecules that are not too large). Thus, for distances of major interest for binding, it is physically correct to use the Schrödinger equation without retardation, and hence Eq. (1.2) is meaningful. For small R, nuclear recoil effects may play a role (see Ref. 13).

The calculation and notation in this paper will seem to the reader to be complex. Actually, the complexity is more apparent than real, and a few words about the strategy of our proof may be helpful. The implementation of the strategy will be given in detail later.

We start with several small units (molecules) which we call clusters. There are $\mathscr{C}$ clusters and $\alpha = 1, 2, \ldots, \mathscr{C}$ designates the cluster. The ground-state energy and wave function of each cluster is e^α and ϕ_0^α. A conveniently chosen point in each cluster, called the "center," is denoted by $\mathbf{R}^\alpha$. The problem is to construct a variational trial function ψ (of all the variables in the system) whose energy is lower than $\sum e^\alpha$ by an amount const$\times \sum (R^{\alpha\beta})^{-6}$.

Step 1: Apply a cutoff to each ϕ_0^α in a large ball centered at $\mathbf{R}^\alpha$, in such a way that the balls are disjoint. By the variational principle the energy must *increase*, but since ϕ_0^α decays exponentially, this increase of the energy will only be by an amount proportional to $\sum \exp(-R_\alpha)$, where R_α is the radius of the cutoff. The cutoff function is denoted by ϕ^α.

Step 2: Let $\psi_{\mathbf{m}}^\alpha = \mathbf{m} \cdot \sum_{i=1}^{n^\alpha} \nabla_i \phi^\alpha$ where n^α is the number of electrons in cluster α and $|\mathbf{m}| = 1$. The trial function is given by

$$\psi = \prod_{\alpha=1}^{\mathscr{C}} \phi^\alpha + \sum_{\substack{\alpha,\beta \\ (1 \le \alpha < \beta \le \mathscr{C})}} \lambda_{\alpha\beta} \psi_{\mathbf{m}_{\alpha\beta}}^\alpha \psi_{\mathbf{n}_{\alpha\beta}}^\beta \prod_{\gamma\,(\neq \alpha,\beta)}'' \phi^\gamma \, . \tag{1.3}$$

The $\lambda_{\alpha\beta}$ are adjustable constants and the $\mathbf{m}_{\alpha\beta}$ and $\mathbf{n}_{\alpha\beta}$ are adjustable vectors. Since $\langle \psi_{\mathbf{m}_{\alpha\beta}}^\alpha | \phi^\alpha \rangle = 0$, the normalization $\langle \psi | \psi \rangle$ will be of the form

$$1 + \sum_{\substack{\alpha,\beta \\ (\alpha < \beta)}} \lambda_{\alpha\beta}^2 \times \text{const} \, .$$

However, $\langle \psi | H \psi \rangle$ will have a cross term proportional to the $\lambda_{\alpha\beta}$ coming from the *inter*cluster Coulomb potential. We should *like* $\langle \psi | H \psi \rangle$ to be of the form

$$\left[\sum\nolimits_\alpha e^\alpha \right] \langle \psi | \psi \rangle + \sum \lambda_{\alpha\beta}^2 \times \text{const} + \sum \lambda_{\alpha\beta} (R^{\alpha\beta})^{-3} \times \text{const} \, .$$

Minimizing the ratio $\langle \psi | H \psi \rangle / \langle \psi | \psi \rangle$ with respect to each $\lambda_{\alpha\beta}$ would then lead (more or less) to $\lambda_{\alpha\beta} \sim (R^{\alpha\beta})^{-3}$ and hence to

$$E < \sum_{\alpha} e^{\alpha} - \text{const} \times \sum_{\substack{\alpha,\beta \\ (\alpha<\beta)}} (R^{\alpha\beta})^{-6} .$$

Step 3: Unfortunately, the intercluster Coulomb interaction is not simply $\lambda_{\alpha\beta}(R^{\alpha\beta})^{-3}$. Its calculation is complicated by the fact that each cluster is not spherically symmetric. To avoid this difficulty and to get a rigorous bound to the $\lambda_{\alpha\beta}$ term, we consider all spatial orientations of the clusters and orientations of the $\mathbf{m}_{\alpha\beta}$ and $\mathbf{n}_{\alpha\beta}$ (which enters in the definition of ψ). By averaging over the orientations of the clusters and also averaging over certain selected orientations of the $\mathbf{m}_{\alpha\beta}$ and $\mathbf{n}_{\alpha\beta}$, a bound of the desired form is obtained. This implies that there exists *some* orientation of the clusters and the **m**'s and **n**'s so that $\langle \psi \mid H\psi \rangle \leq$ (average over orientations) $\leq (\sum e^{\alpha} +$ van der Waals term$) \langle \psi \mid \psi \rangle$.

In any particular case, the wave function ψ which we construct is not the best possible one within the framework of functions of the type (1.3). We use it because we are striving for simplicity and generality—not for good constants in the energy bound.

II. THE GENERAL PROCEDURE

First, some more notation is needed. There are $\mathscr{C}$ clusters indexed by α, $\alpha = 1,2,\ldots,\mathscr{C}$ and $\mathbf{R}^{\alpha} \in \mathbb{R}^3$ denotes the center of the cluster α. $\mathbf{X}_i^{\alpha}$, $i = 1,2,\ldots,M^{\alpha}$ are the coordinates of the nuclei in α relative to $\mathbf{R}^{\alpha}$. This is also denoted collectively by $\underline{X}^{\alpha}$. Similarly, $Z_i^{\alpha} \in \mathbb{N}$ and $\underline{Z}^{\alpha}$ denote the charges of these nuclei. We suppose that all the nuclear coordinates $\underline{X}^{\alpha}$ are contained in a ball, B^{α}, of radius $R_{\alpha} > 0$, centered at $\mathbf{R}^{\alpha}$ and that the $\mathscr{C}$ balls are disjoint. In fact, we can define R_{α} by

$$R_{\alpha} = \tfrac{1}{2} \min_{\substack{\alpha,\beta \\ \beta\neq\alpha}} \{ \mid \mathbf{R}^{\alpha\beta} \mid \} , \qquad (2.1)$$

with $\mathbf{R}^{\alpha\beta} \equiv \mathbf{R}^{\alpha} - \mathbf{R}^{\beta}$. Later on we shall specify how large R_{α} must be in order that our bounds have a simple form.

If only cluster α were present, it would have $n^{\alpha} = \sum_i Z_i^{\alpha}$ electrons to be neutral. The coordinates of these n^{α} electrons (relative to $\mathbf{R}^{\alpha}$) are denoted by $\mathbf{x}_i^{\alpha}$ and collectively by $\underline{x}^{\alpha}$. The wave functions we shall use will be sums of functions of the form $\Phi = \phi^1(\underline{x}^1)\phi^2(\underline{x}^2) \cdots \phi^{\mathscr{C}}(\underline{x}^{\mathscr{C}})$ with $\phi^{\alpha}(\underline{x}^{\alpha}) = 0$ if any x_i^{α} is outside of B^{α}. Each ϕ^{α} satisfies the Pauli principle but Φ does not. (The electron spins should be included but, since they play no essential role, we omit explicit reference to the spins for simplicity of notation.) However, if Φ is antisymmetrized no cross terms appear in $\langle \Phi \mid H\Phi \rangle$ or in $\langle \Phi \mid \Phi \rangle$ (because the B^{α} are disjoint) which means that we can simply ignore the antisymmetrization of Φ. Therefore it makes sense in the full problem to continue to speak of n^{α} electrons being associated with cluster α.

Because of translation invariance, $\mathbf{R}^{\alpha}$ will not appear in the Hamiltonian H^{α} of cluster α but only in the combination $\mathbf{R}^{\alpha\beta} = \mathbf{R}^{\alpha} - \mathbf{R}^{\beta}$ in the interaction between cluster α and cluster β. In atomic units, $\hbar = e = 2m_e = 1$, and, in the above notation, H^{α} is written as

$$\begin{aligned} H^{\alpha} = \sum_{i=1}^{n^{\alpha}} -\Delta_{i,\alpha} + \sum_{\substack{i,k \\ (1\leq i<k\leq n^{\alpha})}} \mid \mathbf{x}_i^{\alpha} - \mathbf{x}_k^{\alpha} \mid^{-1} \\ - \sum_{i=1}^{n^{\alpha}} \sum_{j=1}^{M^{\alpha}} Z_j^{\alpha} \mid \mathbf{x}_i^{\alpha} - \mathbf{X}_j^{\alpha} \mid^{-1} \\ + \sum_{\substack{i,k \\ (1\leq i<k\leq M^{\alpha})}} Z_i^{\alpha} Z_k^{\alpha} \mid \mathbf{X}_i^{\alpha} - \mathbf{X}_k^{\alpha} \mid^{-1} . \end{aligned} \qquad (2.2)$$

The interaction between two clusters again involves an electron-electron, an electron-nucleus, and a nucleus-nucleus interaction,

$$\begin{aligned} V^{\alpha\beta} = \sum_{i,j} \mid \mathbf{x}_i^{\alpha} - \mathbf{x}_j^{\beta} + \mathbf{R}^{\alpha\beta} \mid^{-1} - \sum_{i,j} \mid \mathbf{x}_i^{\alpha} - \mathbf{X}_j^{\beta} + \mathbf{R}^{\alpha\beta} \mid^{-1} Z_i^{\beta} \\ - \sum_{i,j} \mid \mathbf{x}_j^{\beta} - \mathbf{X}_i^{\alpha} + \mathbf{R}^{\alpha\beta} \mid^{-1} Z_i^{\alpha} \\ + \sum_{i,j} \mid \mathbf{X}_i^{\alpha} - \mathbf{X}_j^{\beta} + \mathbf{R}^{\alpha\beta} \mid^{-1} Z_i^{\alpha} Z_j^{\beta} . \end{aligned} \qquad (2.3)$$

The total Hamiltonian consists of H^0, the sum of the cluster Hamiltonians, and the interaction V between them

$$H(\underline{X}^{\alpha}, \underline{R}^{\alpha\beta}) = H^0 + V = \sum_{\alpha=1}^{\mathscr{C}} H^{\alpha} + \sum_{\substack{\alpha,\beta \\ (1\leq\alpha<\beta\leq\mathscr{C})}} V^{\alpha\beta} . \qquad (2.4)$$

To formalize the averaging procedure denote by $\mathscr{R}^{\alpha}\mathbf{X}_k^{\alpha}$ a rotation of the coordinate $\mathbf{X}_k^{\alpha}$ around the center $\mathbf{R}^{\alpha}$ and by $d\mathscr{R}^{\alpha}$ the normalized volume element (Haar measure) of the rotations. We denote $\prod_{\alpha} d\mathscr{R}^{\alpha}$ by $d\mathscr{R}$. What we shall show is that for some trial functions $\psi(\underline{X}^{\alpha}, \underline{m})$, which in addition to the nuclear coordinates also depend on some collection of polarization vectors, $\underline{m}$, we have for sufficiently large $\mid \mathbf{R}^{\alpha\beta} \mid$,

$$\int d\mathscr{R} \sum_{\underline{m}} \left[\langle \psi(\mathscr{R}^{\alpha}\underline{X}^{\alpha},\underline{m}) \mid H(\mathscr{R}^{\alpha}\underline{X}^{\alpha},\underline{R}^{\alpha\beta}) \mid \psi(\mathscr{R}^{\alpha}\underline{X}^{\alpha},\underline{m}) \rangle - \| \psi(\mathscr{R}^{\alpha}\underline{X}^{\alpha},\underline{m}) \|^2 \left[\sum_{\alpha=1}^{\mathscr{C}} e^{\alpha} - \sum_{\substack{\alpha,\beta \\ \alpha>\beta}} v_{\alpha\beta}(\mid \underline{R}^{\alpha\beta} \mid) \right] \right] \leq 0 , \qquad (2.5)$$

where $v_{\alpha\beta}(R) = C_1/(R^6 + C_2)$. We shall use the symbol $\sum_{\underline{m}}$ for an average over the polarization directions, whose precise nature will be given in Sec. VI. Since the average in (2.5) is negative, we reach the conclusion that there are some orientations such that the clusters attract each other at least as much as the van der Waals energy.

III. THE TRIAL FUNCTION

For our results we require the clusters to be clearly separated. By this we mean that the wave functions should not overlap. This, of course, is not true for the ground-state wave functions which decay only exponentially, but may be achieved by a slight adjustment of the wave function which will not cost too much energy. If ϕ_0^α is the (real-valued) ground-state wave function of H^α,

$$H^\alpha \phi_0^\alpha = e^\alpha \phi_0^\alpha \,, \tag{3.1}$$

we shall use a function

$$\phi^\alpha(\underline{x}^\alpha, \underline{X}^\alpha) = \phi_0^\alpha(\underline{x}^\alpha, \underline{X}^\alpha) f(\underline{x}^\alpha) \,, \tag{3.2}$$

where

$$f(\underline{x}^\alpha) = \prod_{k=1}^{n_\alpha} \mathcal{X}(|\mathbf{x}_k^\alpha|) \,, \tag{3.3}$$

where $\mathcal{X}(s)$ is a smooth function which is 1 for $s < R_\alpha - 1$ and 0 for $s > R_\alpha$, and such that $|\mathcal{X}'(s)|, |\mathcal{X}''(s)| \le 4$ for $R_\alpha - 1 < s < R_\alpha$ and zero otherwise. For ϕ^α we have

$$H^\alpha \phi^\alpha = e^\alpha \phi^\alpha - \sum_{k=1}^{n^\alpha} (2\nabla_k^\alpha \phi_0^\alpha \cdot \nabla_k^\alpha f + \phi_0^\alpha \Delta_k^\alpha f) \,, \tag{3.4}$$

and, by some partial integrations,

$$\langle \phi^\alpha | H^\alpha \phi^\alpha \rangle = e^\alpha + \sum_{k=1}^{n^\alpha} \int d\underline{x}^\alpha |\phi_0^\alpha|^2 |\nabla_k^\alpha f|^2 \,, \tag{3.5}$$

where we assumed $\langle \phi^\alpha | \phi^\alpha \rangle = 1$.

The radius R_α was defined in (2.1) and it increases with increasing separation of the clusters. It will turn out that the error in the energy caused by replacing ϕ_0^α by ϕ^α depends only on the single-particle electron density $\rho^\alpha(\mathbf{x})$, defined in the usual way [see (5.2) but omit the spherical average $\int d\mathscr{R}$]. It is known that $\rho^\alpha(\mathbf{x})$ decays exponentially, which means that for some r^α and $c > 0$,

$$\rho^\alpha(\mathbf{x}) < \exp[c(r^\alpha - |\mathbf{x}|)] \quad \text{for } |\mathbf{x}| > r^\alpha \,.$$

We take r^α as the *definition* of the *cluster radius*. The additional terms in (3.4) and (3.5), which involve only the region $R_\alpha - 1 < |x| < R_\alpha$, will thus be exponentially small (as a function of R_α) when $R_\alpha > r^\alpha + 1$.

Next, we need a wave function that describes a polarized cluster and there are many choices possible. We found the most convenient form to be

$$\psi_{\mathbf{m}}^\alpha = \mathbf{m} \cdot \sum_{k=1}^{n^\alpha} \nabla_k^\alpha \phi^\alpha, \quad \mathbf{m} \in \mathbf{R}^3, \ |\mathbf{m}| = 1 \,. \tag{3.6}$$

It is easily seen to be orthogonal to ϕ^α,

$$\langle \psi_{\mathbf{m}}^\alpha | \phi^\alpha \rangle = 0 \,, \tag{3.7}$$

and its norm is the expectation value of the square of the total momentum of all electrons in cluster α in the direction of $\mathbf{m}$,

$$\langle \psi_{\mathbf{m}}^\alpha | \psi_{\mathbf{m}}^\alpha \rangle = \int d\underline{x}^\alpha \left| \mathbf{m} \cdot \sum_{k=1}^{n^\alpha} \nabla_k^\alpha \phi^\alpha \right|^2 \,. \tag{3.8}$$

This quantity still depends on the direction $\mathbf{m}$. However, in our results only the scalar product averaged over rotations of the nuclear coordinates will appear and

$$\int d\mathscr{R} \langle \psi_{\mathbf{m}}^\alpha | \psi_{\mathbf{m}}^\alpha \rangle \equiv \tau^\alpha$$

is independent of $\mathbf{m}$. At the end of the paper we shall collect simple estimates for the various constants such as τ^α which will enter our result. For now we go on to exhibit the trial function ψ for the total system (the products are always in the sense of tensor products)

$$\begin{aligned} \psi = \prod_{\alpha=1}^{\mathscr{C}} \phi^\alpha + \sum_{\substack{\alpha,\beta \\ (1 \le \alpha < \beta \le \mathscr{C})}} & \lambda_{\alpha\beta} \phi^1 \cdots \phi^{\alpha-1} \psi_{\mathbf{m}_{\alpha\beta}}^\alpha \phi^{\alpha+1} \cdots \phi^{\beta-1} \\ & \times \psi_{\mathbf{n}_{\alpha\beta}}^\beta \phi^{\beta+1} \cdots \phi^{\mathscr{C}} \\ \equiv \Phi + \sum_{\substack{\alpha,\beta \\ (\alpha<\beta)}} & \lambda_{\alpha\beta} \psi^{\alpha\beta} \,. \end{aligned} \tag{3.9}$$

Here $\lambda_{\alpha\beta} \in \mathbf{R}$ and $\mathbf{m}_{\alpha\beta}, \mathbf{n}_{\alpha\beta} \in S^2$ are variational parameters to be chosen later. Notice that the polarization vectors $\mathbf{m}$ and $\mathbf{n}$ of the clusters depend on the *pair* of clusters α and β. Because of the orthogonality (3.7) there are no terms linear in the λ's in the norm of ψ,

$$\langle \psi | \psi \rangle = 1 + \sum_{\substack{\alpha,\beta \\ (\alpha<\beta)}} \lambda_{\alpha\beta}^2 \|\psi_{\mathbf{m}_{\alpha\beta}}^\alpha\|^2 \|\psi_{\mathbf{n}_{\alpha\beta}}^\beta\|^2 \,. \tag{3.10}$$

IV. THE EXPECTATION VALUE OF H^0

In calculating $\langle \psi | H^\alpha \psi \rangle$ we first note that the term independent of λ is almost e^α except for the exponentially decreasing contribution in (3.5),

$$\langle \Phi | H^\alpha \Phi \rangle = e^\alpha + \sum_{k=1}^{n^\alpha} \int d\underline{x}^\alpha |\phi_0^\alpha|^2 |\nabla_k^\alpha f|^2 \equiv e^\alpha + b_1^\alpha \,, \tag{4.1}$$

where the boundary term b_1^α will be less than $c\exp(-R_\alpha)$. The orthogonality (3.7) makes the contributions which are linear in λ vanish,

$$\begin{aligned} \langle \Phi | H^\alpha \psi^{\alpha\beta} \rangle &= \langle \phi^\alpha \cdot \phi^\beta | H^\alpha \psi_{\mathbf{m}_{\alpha\beta}}^\alpha \psi_{\mathbf{n}_{\alpha\beta}}^\beta \rangle \\ &= \langle \phi^\alpha | H^\alpha \psi_{\mathbf{m}_{\alpha\beta}}^\alpha \rangle \langle \phi^\beta | \psi_{\mathbf{n}_{\alpha\beta}}^\beta \rangle = 0 \,. \end{aligned} \tag{4.2}$$

The terms quadratic in λ require some rearrangement because we want to compare $\langle \psi | H | \psi \rangle$ with $\|\psi\|^2 \sum_\alpha e^\alpha$ and not just with $\sum_\alpha e^\alpha$, which we get from (4.1). To achieve this we use the following identity, where we momentarily abbreviate $\sum_{k=1}^{n^\alpha} \mathbf{m} \cdot \nabla_k^\alpha$ by $P^\alpha = -(P^\alpha)^*$,

$$\begin{aligned} \langle \psi^{\alpha\beta} | H^\alpha | \psi^{\alpha\beta} \rangle \\ &= -\langle \phi^\alpha | P^\alpha H^\alpha P^\alpha | \phi^\alpha \rangle \|\psi_{\mathbf{n}_{\alpha\beta}}^\beta\|^2 \\ &= -\tfrac{1}{2} \langle \phi^\alpha | [P^\alpha, [H^\alpha, P^\alpha]] + H^\alpha (P^\alpha)^2 + (P^\alpha)^2 H^\alpha | \phi^\alpha \rangle \\ &\quad \times \|\psi_{\mathbf{n}_{\alpha\beta}}^\beta\|^2 \,. \end{aligned} \tag{4.3}$$

Using (3.4), $-H^\alpha (P^\alpha)^2 - (P^\alpha)^2 H^\alpha$ indeed yields $e^\alpha \|\psi^{\alpha\beta}\|^2$

and some boundary terms, which we call b_2^α, and which are also exponentially decreasing. As regards the double commutator, we first see from (2.2) that the only term in H^α that is not invariant under a common displacement of all electrons is the electron-nucleus attraction

$$[P^\alpha,H^\alpha]=-\sum_{k,j}\mathbf{m}_{\alpha\beta}\cdot\nabla_k^\alpha Z_j^\alpha\,|\,\mathbf{x}_k^\alpha-\mathbf{X}_j^\alpha\,|^{-1}\,, \tag{4.4}$$

$$[P^\alpha,[P^\alpha,H^\alpha]]=-\sum_{k,j}(\mathbf{m}_{\alpha\beta}\cdot\nabla_k^\alpha)^2 Z_j^\alpha\,|\,\mathbf{x}_k^\alpha-\mathbf{X}_j^\alpha\,|^{-1}\,. \tag{4.5}$$

A further simplification of the expectation value of this expression results if we carry out the integrations $\int d\mathscr{R}^\alpha \int d\mathscr{R}^\beta$. The integration $\int d\mathscr{R}^\beta$ makes $||\psi_{\mathbf{n}_{\alpha\beta}}^\beta||^2$ independent of $\mathbf{n}_{\alpha\beta}$ and $\int d\mathscr{R}^\alpha$ makes the expectation value of (4.5) independent of $\mathbf{m}_{\alpha\beta}$. The reason is that after rotating the nuclei there is no distinguished direction left. Since the result is independent of $\mathbf{m}_{\alpha\beta}$, we may freely average over three orthogonal directions of $\mathbf{m}_{\alpha\beta}$ and thus replace $-(\mathbf{m}\cdot\nabla_k^\alpha)^2$ by $-\frac{1}{3}\Delta_k^\alpha$ which just gives $(4\pi/3)\delta(\mathbf{x}_k^\alpha-\mathbf{X}_j^\alpha)$ in (4.5). Upon collecting the contributions we end up with

$$\begin{aligned}\int d\mathscr{R}^\alpha \int d\mathscr{R}^\beta\langle\psi^{\alpha\beta}\,|\,H^\alpha\,|\,\psi^{\alpha\beta}\rangle&=e^\alpha||\psi^{\alpha\beta}||^2+\left[b_2^\alpha+\frac{2\pi}{3}\sum_{k,j}\langle\phi^\alpha\,|\,Z_j^\alpha\delta(\mathbf{x}_k^\alpha-\mathbf{X}_j^\alpha)\,|\,\phi^\alpha\rangle\right]\tau^\beta\\&\equiv e^\alpha||\psi^{\alpha\beta}||^2+(b_2^\alpha+Q^\alpha)\tau^\beta\end{aligned} \tag{4.6}$$

where Q^α is $2\pi/3$ times the sum of the electron densities at the nuclei in cluster α.

V. THE EXPECTATION VALUE OF V

For the evaluation of $\langle\psi\,|\,V\,|\,\psi\rangle$ we shall heavily use Newton's theorem according to which the potential of a spherically symmetric charge distribution with net charge zero vanishes outside the support of this charge distribution. This theorem makes the $\langle\Phi\,|\,V\,|\,\Phi\rangle$ term vanish upon rotation of the nuclei because it becomes the electrostatic interaction between two nonoverlapping spherical charge distributions of net charge zero. To demonstrate this formally we note that

$$\int d\mathscr{R}\langle\Phi(\underline{x},\mathscr{R}\underline{X})\,|\,V(\underline{x},\mathscr{R}\underline{X})\,|\,\Phi(\underline{x},\mathscr{R}\underline{X})\rangle$$

is a sum of terms

$$\int d\mathscr{R}^\alpha \int d\mathscr{R}^\beta\langle\phi^\alpha(\underline{x}^\alpha,\mathscr{R}^\alpha\underline{X}^\alpha)\phi^\beta(\underline{x}^\beta,\mathscr{R}^\beta\underline{X}^\beta)\,|\,V^{\alpha\beta}(\underline{x}^\alpha,\underline{x}^\beta,\mathscr{R}^\alpha\underline{X}^\alpha,\mathscr{R}^\beta\underline{X}^\beta,\mathbf{R}^{\alpha\beta})\,|\,\phi^\alpha(\underline{x}^\alpha,\mathscr{R}^\alpha\underline{X}^\alpha)\phi^\beta(\underline{x}^\beta,\mathscr{R}^\beta\underline{X}^\beta)\rangle\,. \tag{5.1}$$

They involve only the one-electron density which upon integrating over $\mathscr{R}$ becomes spherically symmetric (around the center R^α) since $\phi^\alpha(\underline{x}^\alpha,\mathscr{R}^\alpha\underline{X}^\alpha)=\phi^\alpha((\mathscr{R}^\alpha)^{-1}\underline{x}^\alpha,\underline{X}^\alpha)$. The one-electron density is

$$\rho^\alpha(\mathbf{x}_1^\alpha)\equiv n^\alpha\int d\mathscr{R}^\alpha\int dx_2^\alpha\cdots\int dx_{n^\alpha}^\alpha\,|\,\phi^\alpha(\mathbf{x}_1^\alpha,\mathbf{x}_2^\alpha,\ldots,\mathbf{x}_{n^\alpha}^\alpha,\mathscr{R}^\alpha\underline{X}^\alpha)\,|^2\,. \tag{5.2}$$

For $|\,\mathbf{x}\,|<R^\alpha-1$, we have $\rho^\alpha(\mathbf{x})=[1+C\exp(-R_\alpha)]\rho_0^\alpha(\mathbf{x})$ for some $C>0$, where $\rho_0^\alpha(\mathbf{x})$ is the "true" electron density calculated with ϕ_0^α.

With the averaged nuclear charge

$$n^\alpha(\,|\,\mathbf{x}\,|\,)=\int d\mathscr{R}^\alpha\sum_{j=1}^{M^\alpha}\delta(\mathbf{x}-\mathscr{R}^\alpha\mathbf{X}_j^\alpha)\,, \tag{5.3}$$

and similar definitions for cluster β, (5.1) becomes

$$\int d\mathbf{x}\int d\mathbf{y}\,[\rho^\alpha(\mathbf{x})-n^\alpha(\mathbf{x})][\rho^\beta(\mathbf{y})-n^\beta(\mathbf{y})]\,|\,\mathbf{x}-\mathbf{y}+\mathbf{R}^{\alpha\beta}\,|^{-1}=0\,. \tag{5.4}$$

In the terms proportional to λ we have the factor $\phi^\alpha P^\alpha\phi^\alpha=\frac{1}{2}P^\alpha(\phi^\alpha)^2$. After partial integration, the gradient acts on the potential, and thus we obtain the dipole-dipole interaction directly:

$$\begin{aligned}&\int d\mathscr{R}^\alpha\int d\mathscr{R}^\beta\langle\phi^\alpha\cdot\phi^\beta\,|\,V^{\alpha\beta}\,|\,\psi^\alpha\cdot\psi^\beta\rangle\\&\quad=\int d\mathscr{R}^\alpha\int d\mathscr{R}^\beta\int d\underline{x}^\alpha\int d\underline{x}^\beta\tfrac{1}{4}\sum_i\mathbf{m}_{\alpha\beta}\cdot\nabla_i^\alpha\,|\,\phi^\alpha(\underline{x}^\alpha,\mathscr{R}^\alpha\underline{X}^\alpha)\,|^2\sum_j\mathbf{n}_{\alpha\beta}\cdot\nabla_j^\beta\,|\,\phi^\beta(\underline{x}^\beta,\mathscr{R}^\beta\underline{X}^\beta)\,|^2V(\underline{x}^\alpha,\underline{x}^\beta,\mathscr{R}^\alpha\underline{X}^\alpha,\mathscr{R}^\beta\underline{X}^\beta,\mathbf{R}^{\alpha\beta})\\&\quad=\tfrac{1}{4}\int d\mathbf{x}\int d\mathbf{y}\,\rho^\alpha(\mathbf{x})\rho^\beta(\mathbf{y})(\mathbf{m}_{\alpha\beta}\cdot\nabla_{\mathbf{x}})(n_{\alpha\beta}\cdot\nabla_{\mathbf{y}})\,|\,\mathbf{x}-\mathbf{y}+\mathbf{R}^{\alpha\beta}\,|^{-1}\\&\quad=\tfrac{1}{4}n^\alpha n^\beta[3(\mathbf{m}_{\alpha\beta}\cdot\mathbf{R}^{\alpha\beta})(\mathbf{n}_{\alpha\beta}\cdot\mathbf{R}^{\alpha\beta})-(\mathbf{m}_{\alpha\beta}\cdot\mathbf{n}_{\alpha\beta})\,|\,\mathbf{R}^{\alpha\beta}\,|^2]\,|\,\mathbf{R}^{\alpha\beta}\,|^{-5}\,.\end{aligned} \tag{5.5}$$

Newton's theorem has been used again in order to perform the $d\mathbf{x}$ and $d\mathbf{y}$ integrations. The contribution $\langle \psi^{\alpha\beta} | V^{\alpha\beta} | \psi^{\alpha\beta} \rangle$ is analogous to the term $\langle \phi | V^{\alpha\beta} | \phi \rangle$ except that the one-electron density is now calculated with $\psi^{\alpha} = \mathbf{m} \cdot \sum_{j=1}^{n^{\alpha}} \nabla_j^{\alpha} \phi^{\alpha}$ instead of ϕ^{α}. If we call this density $\rho_{\mathbf{m}}^{\alpha}(\mathbf{x})$ it will not be spherically symmetric, but $\rho_{\mathscr{R}\mathbf{m}}^{\alpha}(\mathscr{R}\mathbf{x}) = \rho_{\mathbf{m}}^{\alpha}(\mathbf{x})$. Since it is quadratic in $\mathbf{m}$ it must be of the form $|\mathbf{m}|^2 f_1(|\mathbf{x}|) + (\mathbf{m} \cdot \mathbf{x})^2 f_2(|\mathbf{x}|)$. Adding in the averaged charge of the nuclei will give a charge distribution $Q(x)$ with no net charge, and no dipole moment since $Q(x) = Q(-x)$. However, it may have a quadrupole moment and we may pick up a term

$$\langle \psi^{\alpha\beta} | V^{\alpha\beta} | \psi^{\alpha\beta} \rangle = c^{\alpha\beta} |\mathbf{R}^{\alpha\beta}|^{-5} \tag{5.6}$$

of unknown sign.

VI. CHOICE OF THE POLARIZATION DIRECTIONS

Our goal is to make the term proportional to λ, which will be negative for a suitable choice of λ, as big as possible while the term proportional to λ^2 should be kept small. Only (5.5) contributes linearly in λ and its maximal value $2n^{\alpha}n^{\beta}|\mathbf{R}^{\alpha\beta}|^{-3}$ is reached if we choose $\mathbf{m}_{\alpha\beta}$ and $\mathbf{n}_{\alpha\beta}$ in the direction of $\mathbf{R}^{\alpha\beta}$. However, this leaves us with the quadrupole term (5.6). We can get rid of the latter if we average over $\mathbf{m}_{\alpha\beta}$ and $\mathbf{n}_{\alpha\beta}$ in the following way. Let

$$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$$

be the unit vector in the direction of $\mathbf{R}^{\alpha\beta}$ and

$$\begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

two directions completing the orthogonal basis. Then average the polarizations over the following nine pairs of vectors:

$$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}; \quad \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix}; \quad \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ -1 \end{bmatrix};$$

$$\begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}; \quad \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix}; \quad \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ -1 \end{bmatrix};$$

$$\begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}, \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}; \quad \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}, \begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix}; \quad \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ -1 \end{bmatrix}.$$

In this way the quadrupole term (5.6) vanishes since $Q(x)$ becomes spherically symmetric. On the other hand (5.5) averages to $\frac{1}{9}n^{\alpha}n^{\beta}|\mathbf{R}^{\alpha\beta}|^{-3}$. Since λ will be proportional to R^{-3} the quadrupole term (5.6) will contribute to the order R^{-11} and the first choice (i.e., no averaging) will give a better estimate for large R. On the other hand, for smaller distances averaging may be better, as (5.6) is not easy to estimate accurately.

VII. CHOICE OF THE $\lambda_{\alpha\beta}$

So far we have evaluated expressions such as $\langle \psi^{\alpha\beta} | V^{\alpha'\beta'} | \psi^{\alpha''\beta''} \rangle$ where all three index pairs $(\alpha\beta)$, $(\alpha'\beta')$, and $(\alpha''\beta'')$ are equal. The orthogonality (3.7) insures that terms in which they are not equal vanish. Similarly $\langle \psi^{\alpha\beta} | H^{\gamma} | \psi^{\alpha'\beta'} \rangle$ is not zero only if $(\alpha\beta) = (\alpha'\beta')$ and γ is either α or β. Thus collecting our results we arrive at

$$\sum_{\underline{m}} \int d\mathscr{R} \langle \psi | H | \psi \rangle = \sum_{\underline{m}} \int d\mathscr{R} \left[\sum_{\alpha=1}^{\mathscr{C}} \left[e^{\alpha} \|\psi\|^2 + \sum b_1^{\alpha} \right] + \frac{1}{9} \sum_{\substack{\alpha,\beta \\ (1 \le \alpha < \beta \le \mathscr{C})}} \lambda_{\alpha\beta} n^{\alpha} n^{\beta} |\mathbf{R}^{\alpha\beta}|^{-3} \right.$$
$$\left. + \sum_{\substack{\alpha,\beta \\ (1 \le \alpha < \beta \le \mathscr{C})}} \lambda_{\alpha\beta}^2 [(b_2^{\alpha} + Q^{\alpha})\tau^{\beta} + (b_2^{\beta} + Q^{\beta})\tau^{\alpha}] \right] . \tag{7.1}$$

To get an upper bound for the energy we have to extract a factor $\|\psi\|^2 = 1 + \sum_{\alpha<\beta} \lambda_{\alpha\beta}^2 \tau_{\alpha} \tau_{\beta}$ from the term in large square brackets. The minimization with respect to the $\lambda_{\alpha\beta}$'s then leads to a coupled system of cubic equations which cannot be solved analytically. For our purpose, however, it is sufficient to minimize the last two terms by putting

$$\lambda_{\alpha\beta} = -\tfrac{1}{18} n^{\alpha} n^{\beta} |\mathbf{R}^{\alpha\beta}|^{-3} [(Q^{\alpha} + b_2^{\alpha})\tau^{\beta} + (Q^{\beta} + b_2^{\beta})\tau^{\alpha}]^{-1} . \tag{7.2}$$

By extracting

$$\|\psi\|^2 = 1 + \frac{1}{(18)^2} \sum (n^{\alpha} n^{\beta})^2 \tau^{\alpha} \tau^{\beta} |\mathbf{R}_{\alpha\beta}|^{-6} [(Q^{\alpha} + b_2^{\alpha})\tau^{\beta} + (Q^{\beta} + b_2^{\beta})\tau^{\alpha}]^{-2} ,$$

we obtain

$$\sum_{m} \int d\mathscr{R} \langle \psi | H | \psi \rangle = \sum_{\underline{m}} \int d\mathscr{R} ||\psi||^2 \left[\sum_{\alpha=1}^{\mathscr{C}} (e^\alpha + b_1^\alpha / ||\psi||^2) - \sum_{\substack{\alpha,\beta \\ (1 \le \alpha < \beta \le \mathscr{C})}} \frac{(n^\alpha n^\beta)^2}{(18)^2[(Q^\alpha + b_1^\alpha)\tau^\beta + (Q^\beta + b_2^\beta)\tau^\alpha]} \times \left[|\mathbf{R}^{\alpha\beta}|^6 + \sum_{\substack{\sigma,\rho \\ (1 \le \sigma < \rho \le \mathscr{C})}} \frac{(n^\sigma n^\rho)^2 \tau^\sigma \tau^\rho}{(18)^2[(Q^\sigma + b_2^\sigma)\tau^\rho + (Q^\rho + b_2^\rho)\tau^\sigma]} \right]^{-1} \right] . \tag{7.3}$$

Taking $\mathbf{m}_{\alpha\beta}$ and $\mathbf{n}_{\alpha\beta}$ in the direction of $\mathbf{R}^{\alpha\beta}$ would change the factor $(18)^2$ into 4^2 and add $c^{\alpha\beta}|\mathbf{R}^{\alpha\beta}|^{-5}$ to $(Q^\alpha + b_2^\alpha)\tau^\beta + (Q^\beta + b_2^\beta)\tau^\alpha$.

VIII. SOME ESTIMATES

Our result (7.3) contains two parameters, the squared center-of-mass momentum τ, and Q, the density of the electrons at the nuclei. For the former we have the trivial estimate (where T^α is the kinetic energy in the ground state)

$$\tau^\alpha \le n^\alpha \left\langle \phi^\alpha \left| - \sum_{k=1}^{n^\alpha} \Delta_k^\alpha \right| \phi^\alpha \right\rangle \equiv n^\alpha T^\alpha . \tag{8.1}$$

From the stability of matter one knows that for states of negative energy the kinetic energy is bounded by n^α,[14] so that $\tau^\alpha \le c(n^\alpha)^2$. We *conjecture* that actually $\tau^\alpha \le T^\alpha$. Similarly, for the Q^α the bound from Ref. 15 for the atomic case can be extended to the molecular case to give

$$Q^\alpha \le \tfrac{1}{3} \sum_{k,j} \langle \phi^\alpha | Z_j^\alpha | x_k^\alpha - X_j^\alpha |^{-2} | \phi^\alpha \rangle . \tag{8.2}$$

Using the fact that $|\mathbf{x}|^{-2} \le -4\Delta$, the right side of (8.2) can be bounded by the kinetic energy. Again, keeping $\max_{\alpha,j}\{Z_j^\alpha\}$ fixed, we get a bound proportional to $(n^\alpha)^2$, whereas we *conjecture* it should be proportional to n^α. From the *proven* bounds the coefficient in front of the large parentheses in (7.3) becomes independent of the n^α. For the *conjectured* bounds it would be proportional to $n^\alpha n^\beta$, thereby indicating a linearity of the van der Waals forces with respect to the electron number in each cluster.

If one calculates our constants τ and Q for a hydrogen atom one gets a constant in front of R^{-6} which is about an order of magnitude below the known constant for the van der Waals force between two hydrogen atoms. The reason is that our way of generating polarization by a rigid shift is a rather brutal act. In particular, shifting the electrons near the nucleus is energetically costly; it is much better to adjust only the outer parts of the electron cloud. The best way to do this will depend on the exact shape of the cluster, and a simple, general bound which is numerically good in all cases seems to be beyond reach. Our result shows that irrespective of these details one can always get some R^{-6} attraction by a rigid shift.

It will be noted that the factor in large parentheses in (7.3) contains a constant term, $\sum$, in addition to $|\mathbf{R}^{\alpha\beta}|^6$. While this term is asymptotically negligible for large $|\mathbf{R}^{\alpha\beta}|$, it unfortunately grows with $\mathscr{C}$. Our result is therefore useless if $\mathscr{C}$ is very large, e.g., in a crystal where $\mathscr{C} \sim 10^{23}$. To circumvent this difficulty a better trial function Ψ is needed. We believe that the following choice is adequate, but we have not actually pursued the matter: Define the "operator" $D^{\alpha\beta}$ by $D^{\alpha\beta}\phi^\alpha\phi^\beta = \psi^\alpha\psi^\beta, D^{\alpha\beta}\phi^\alpha\psi^\beta = D^{\alpha\beta}\psi^\alpha\phi^\beta = D^{\alpha\beta}\psi^\alpha\psi^\beta = 0$. Then a natural generalization of (3.9) is

$$\Psi = \prod_{\substack{\alpha,\beta \\ (\alpha<\beta)}} (1 + \lambda_{\alpha\beta} D^{\alpha\beta}) \prod_{\alpha=1}^{\mathscr{C}} \phi^\alpha(\underline{x}^\alpha, \underline{X}^\alpha) . \tag{8.3}$$

ACKNOWLEDGMENTS

This work was partially supported by U.S. National Science Foundation Grant No. PHY-81-16101-A03.

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