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Simplified method for calculating the energy of weakly interacting fragments

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A method for calculating approximately the coupling energy of weakly interacting fragments is presented. The method is a simplified version of the density-functional scheme of Kohn and Sham and is applicable whenever the electron density of the coupled fragments does not deviate too markedly from a sum of isolated fragment densities. The coupling energy is expressed directly in terms of properties of the isolated fragments and the only nontrivial computational step is the determination of an eigenvalue sum for the coupled system with a fixed potential. Neither self-consistency cycling nor a solution of Poisson's equation for the coupled fragments is required. The method is therefore particularly appropriate when full density-functional calculations are tractable for the isolated fragments but difficult for the coupled system, e.g., a molecule interacting with a surface. Explicit calculations for dimers illustrate that the approach is very accurate for weakly interacting systems, and that reasonable results can be obtained even for strong covalent bonds.

I. INTRODUCTION

The usefulness of the Kohn-Sham scheme[1] for calculating ground-state energies in molecules and solids has been amply documented over the past decade. Because the scheme is based on an independent-electron wave equation it has physical appeal, and calculations are simper than those required by traditional quantum-chemical methods. It is nevertheless difficult to carry through a full Kohn-Sham calculation for, e.g., a molecule interacting with a surface. This is because the boundary conditions appropriate to the individual units that are to be coupled are different. In practice, the solution of Poisson's equation and the evaluation of the total energy to the desired accuracy are two major obstacles. The purpose of this paper is to introduce a new approximate scheme for calculating the interaction energy of two fragments which circumvent these difficulties. The approximation is almost (but not quite) equivalent to expanding the Kohn-Sham energy expression about a density that is the sum of overlapped but frozen fragment densities and neglecting corrections that are quadratic in the difference density. The resulting energy expression requires the evaluation of some simple overlap integrals of the frozen fragment densities and potentials and the determination of an eigenvalue sum for a potential constructed from the frozen densities. Self-consistency cycling is eliminated and a solution of Poisson's equation for the coupled fragments is not required. The simplicity of the energy expression also assists in the interpretation of results.

The idea of expressing the energy in terms of frozen atomic densities was proposed previously[2] in connection with a Thomas-Fermi-Dirac description of interactions between closed-shell atoms and ions. The present scheme is different from this work in that (i) the energy expression is derived from the density-functional equations, i.e., is not merely postulated, and (ii) the kinetic energy is treated in the manner of Kohn-Sham rather than Thomas-Fermi. The second point is particularly important because it allows a description of bonding in general and is not restricted to interactions between closed shells. The Thomas-Fermi approach fails in this respect because the approximation for the kinetic energy ignores the orbital structure of the configuration. The new scheme is the simplest possible generalization of the earlier work and is semiquantitative, as I will show, even for such strong bonds as that of the N_2 molecule.

The remainder of this paper is organized as follows. In Sec. II I make some general remarks about Kohn-Sham theory and derive the energy expression referred to above. In Sec. III contact is made with the Thomas-Fermi-Dirac approach and the way in which the new approximation describes bonding of different types is described. In Sec. IV some calculations for dimers illustrate the level of accuracy that is to be expected in practice. Finally, in Sec. V, I summarize the main points of the paper. Unless otherwise stated, atomic units will be assumed throughout.

II. DERIVATION OF THE ENERGY EXPRESSION

The Kohn-Sham scheme for calculating energies is based on the expression

$$E = T_0 + \int d\mathbf{x}\, n(\mathbf{x})[\tfrac{1}{2}\phi(\mathbf{x}) + V_{\text{ext}}(\mathbf{x})] + E_{\text{xc}} + E_N \ , \tag{2.1}$$

where E is the total energy for N electrons in nuclear field $V_{\text{ext}}(\mathbf{x})$, $n(\mathbf{x})$, and $\phi(\mathbf{x})$ are the electron density and associated Poisson potential, E_N is the internuclear repulsion, T_0 is the kinetic energy of a system of independent electrons having density $n(\mathbf{x})$, and E_{xc} is the so-called exchange-correlation energy. E and T_0 were shown to be functionals of $n(\mathbf{x})$ so that E_{xc} is also a functional of $n(\mathbf{x})$. The energy of the system is to be determined by varying $n(\mathbf{x})$ in (2.1) to minimize E. This is done in practice by solving an independent-electron wave equation

$$[-\tfrac{1}{2}\nabla^2 + V(\mathbf{x}) - \epsilon_n]\psi_n(\mathbf{x}) = 0 \ , \tag{2.2}$$

where $V(\mathbf{x})$ is an arbitrary potential, constructing T_0 and $n(\mathbf{x})$ from the eigenfunctions of (2.2),

$$T_0=\int d\mathbf{x}\sum_n a_n\psi_n^*(\mathbf{x})(-\tfrac{1}{2}\nabla^2)\psi_n(\mathbf{x})\ , \tag{2.3}$$

$$n(\mathbf{x})=\sum_n a_n\psi_n^*(\mathbf{x})\psi_n(\mathbf{x})\ , \tag{2.4}$$

where a_n are occupation numbers, and evaluating E. The potential $V(\mathbf{x})$ is then varied and the process repeated until the minimum of E is found. The potential and density at minimum, $V_0(\mathbf{x})$, $n_0(\mathbf{x})$, will then be found to satisfy the self-consistency condition

$$V_0(\mathbf{x})=\phi(\mathbf{x})+V_{\text{ext}}(\mathbf{x})+\left.\frac{\delta E_{\text{xc}}}{\delta n(\mathbf{x})}\right|_{n=n_0}\ , \tag{2.5}$$

and this is used to guide the potential towards its minimum value by iteration.

Subject to some representability requirements,[3] the Kohn-Sham scheme is formally exact. Furthermore, an exact expression for E_{xc} can be written down if one invokes the adiabatic connection formulation of the theory,[4] where (2.1) is viewed as a functional of the one-electron potential, $V(\mathbf{x})$, in (2.2). The link between E_{xc} and the density is then implicit and, e.g., the functional derivative in (2.5) is given by

$$\mu_{\text{xc}}(\mathbf{x})=\frac{\delta E_{\text{xc}}}{\delta n(\mathbf{x})}=\int d\mathbf{x}'\frac{\delta E_{\text{xc}}}{\delta V(\mathbf{x}')}\frac{\delta V(\mathbf{x}')}{\delta n(\mathbf{x})}\ . \tag{2.6}$$

If a local-density approximation (LDA) is invoked,

$$E_{\text{xc}}\simeq\int d\mathbf{x}\,n(\mathbf{x})\epsilon_{\text{xc}}(n(\mathbf{x}))\ , \tag{2.7}$$

so that (2.6) reduces to the standard result

$$\mu_{\text{xc}}(\mathbf{x})=\epsilon_{\text{xc}}(n(\mathbf{x}))+n(\mathbf{x})\frac{d\epsilon_{\text{xc}}(n(\mathbf{x}))}{dn(\mathbf{x})}\ , \tag{2.8}$$

the dependence of E_{xc} and μ_{xc} on the orbital structure is lost.[5] However, the kinetic energy T_0 does have such a dependence and this is the reason why, unlike Thomas-Fermi-Dirac theory, the Kohn-Sham scheme describes all kinds of chemical behavior. The success of the LDA in practice suggests that the dependence of E_{xc} on the orbital structure is not critical. Nevertheless, better approximations are needed and, in anticipation that these will become available, the following formal development is general and not restricted to the LDA.

Consider two fragments, F_1 and F_2, whose coupling energy is of interest. Let $n_1(\mathbf{x})$ and $n_2(\mathbf{x})$ be the densities that correspond to the exact minimum of (2.1) for the isolated fragments. These are given by (2.4) for some orbitals and occupations such that (2.2) and (2.5) are satisfied simultaneously. The energy of fragment F_1 can then be written in terms of the self-consistent eigenvalues ϵ_n^1 and density $n_1(\mathbf{x})$

$$E_1=\sum_n^{1} a_n^1\epsilon_n^1-\int d\mathbf{x}\,n_1(\mathbf{x})[\tfrac{1}{2}\phi_1(\mathbf{x})+\mu_{\text{xc}}^{n_1}(\mathbf{x})]+E_{\text{xc}}[n_1]+E_N^1 \tag{2.9}$$

with a similar expression for fragment F_2. Suppose we place the fragments some finite distance R apart (R may involve relative orientation as well as distance) and solve the self-consistency equations exactly, obtaining density $n(\mathbf{x})$, occupations and eigenvalues a_n,ϵ_n, and energy

$$E_R=\sum_n a_n\epsilon_n-\int d\mathbf{x}\,n(\mathbf{x})[\tfrac{1}{2}\phi(\mathbf{x})+\mu_{\text{xc}}^{n}(\mathbf{x})]+E_{\text{xc}}[n]+E_N^R\ . \tag{2.10}$$

Write now

$$n(\mathbf{x})=n_f(\mathbf{x})+\delta n(\mathbf{x})\ , \tag{2.11}$$

with $n_f(\mathbf{x})=n_1(\mathbf{x})+n_2(\mathbf{x})$ with the two frozen fragment densities placed at separation R, and assume $\delta n(\mathbf{x})$ to be sufficiently small that quadratic corrections can be ignored. Introduce a potential

$$\widetilde{V}(\mathbf{x})=\phi_f(\mathbf{x})+\mu_{\text{xc}}^{n_f}(\mathbf{x})+V_{\text{ext}}(\mathbf{x})\ , \tag{2.12}$$

where $V_{\text{ext}}(\mathbf{x})$ is the true external field for separation R and ϕ_f and $\mu_{\text{xc}}^{n_f}$ are computed from the overlapped fragment densities.[6] Then the difference between the true self-consistent potential and $\widetilde{V}(\mathbf{x})$ is

$$\Delta V(\mathbf{x})=\phi(\mathbf{x})-\phi_f(\mathbf{x})+\mu_{\text{xc}}^{n}(\mathbf{x})-\mu_{\text{xc}}^{n_f}(\mathbf{x})\ , \tag{2.13}$$

which will be assumed small. If $\tilde{\epsilon}_n$ are the eigenvalues corresponding to $\widetilde{V}(\mathbf{x})$, we have

$$\sum_n a_n\epsilon_n=\sum_n a_n\tilde{\epsilon}_n+\int d\mathbf{x}\,n(\mathbf{x})\Delta V(\mathbf{x})+O(\Delta V^2)\ , \tag{2.14}$$

which, on substituting in (2.10), gives

$$E_R\simeq\sum_n a_n\tilde{\epsilon}_n+\int d\mathbf{x}\,n(\mathbf{x})[\tfrac{1}{2}\phi(\mathbf{x})-\phi_f(\mathbf{x})-\mu_{\text{xc}}^{n_f}(\mathbf{x})]+E_{\text{xc}}[n]+E_N^R\ . \tag{2.15}$$

Using

$$E_{\text{xc}}[n]=E_{\text{xc}}[n_f]+\int d\mathbf{x}\,\mu_{\text{xc}}^{n_f}(\mathbf{x})\delta n(\mathbf{x})+O(\delta n^2) \tag{2.16}$$

and noting that ϕ is linear in n, we then find

$$E_R\simeq\sum_n a_n\tilde{\epsilon}_n-\int d\mathbf{x}\,n_f(\mathbf{x})[\tfrac{1}{2}\phi_f(\mathbf{x})+\mu_{\text{xc}}^{n_f}(\mathbf{x})]+E_{\text{xc}}[n_f]+E_N^R\ , \tag{2.17}$$

with corrections of order $(\delta n)^2$ and $(\delta V)^2$. This is the desired approximation and involves only the frozen fragment densities and the eigenvalues of (2.2) with a potential $\widetilde{V}(\mathbf{x})$ constructed from these densities.

The absence of a term explicitly linear in the difference density, δn, is of course due ultimately to the variational principle obeyed by E, and it can be seen that (2.17) amounts merely to evaluating (2.10) with n replaced by n_f in this equation and in the one-electron equations (2.2) and (2.5) defining the ϵ_n. Nevertheless, (2.17) does *not* give $E[n_f]$ in the Kohn-Sham sense because the evaluation of this quantity requires knowledge of the one-electron potential that generates density n_f. Similarly, (2.17) does not give $E[\widetilde{V}]$ in the adiabatic-connection sense because the potential $\tilde{V}$ certainly does not generate density n_f. Thus, although the error in using (2.17) in place of (2.1) is strictly quadratic in δn and δV, its sign cannot be deduced from the variational principle.

If the two fragments are stable at $R=\infty$ in the sense that no unfilled levels of one lie beneath filled levels of the other, then the energy (2.17) goes continuously to the sum of isolated fragment energies, E_1 and E_2, as $R \rightarrow \infty$. This may then be subtracted off to give the net binding energy directly,

$$\delta E_R = \sum_n a_n \delta\tilde{\epsilon}_n + \delta E_N^R - \int d\mathbf{x}\, n_1(\mathbf{x})\phi_2(\mathbf{x}) + \delta E_{\mathrm{xc}}^R + \int dx [n_1(x)\mu_{\mathrm{xc}}^{n_1}(x) + n_2(x)\mu_{\mathrm{xc}}^{n_2}(x) - n_f(x)\mu_{\mathrm{xc}}^{n_f}(x)] \; . \tag{2.18}$$

Here δE_N^R represents those terms in the internuclear repulsion where the two nuclei are in different fragments while

$$\delta E_{\mathrm{xc}}^R = E_{\mathrm{xc}}[n_f] - E_{\mathrm{xc}}[n_1] - E_{\mathrm{xc}}[n_2] \; . \tag{2.19}$$

If the two fragments are not stable at $R=\infty$ in the above sense and cannot be made stable trivially by, for example, starting with ionized rather than neutral fragments, then E_R will not go over to the correct asymptotic energy. It may still be possible to describe energy variations within the bonding region however, the crucial criterion being the smallness of $\delta n(\mathbf{x})$ in (2.11). If appropriate "fragment densities" n_1 and n_2 can be found such that $\delta n(\mathbf{x})$ is sufficiently small over a range of R values, then (2.17) will give a good approximation to the energy variation over this range, regardless of its absolute value. Note, in this connection, that the above approach can be applied to the differential $E_{R+dR} - E_R$ in a manner similar to that of Andersen, Skriver, and Nohl.[7] The resulting force formula is particularly useful in closed-packed metal structures and is exact because quadratic corrections do not contribute to the force. The result (2.18) for a quantity that is not a differential will always show an error due to quadratic corrections whose magnitude can only be established by explicit calculation.

In concluding this section I show that core electron eigenvalue shifts can be eliminated from (2.18) on invoking the approximation of frozen, nonoverlapping core wave functions. In this approximation the sum of eigenvalue shifts corresponding to core functions on fragment F_1 is simply

$$\sum_n^{\mathrm{core}_1} \delta\tilde{\epsilon}_n = \int d\mathbf{x}\, n_1^c(\mathbf{x})[\tilde{V}(\mathbf{x}) - V_1(\mathbf{x})] \; , \tag{2.20}$$

where $n_1^c(\mathbf{x})$ is the core density of F_1, $\tilde{V}(\mathbf{x})$ the potential (2.12), and $V_1(\mathbf{x})$ is the potential of fragment F_1. With the use of (2.20) and the analogous expression for F_2 in (2.18), this equation can be reduced to

$$\delta E_R = \sum_n^{v} a_n \delta\tilde{\epsilon}_n + \delta E_N^v - \int d\mathbf{x}\, n_1^v(\mathbf{x})\phi_2^v(\mathbf{x}) + \delta E_{\mathrm{xc}}^R - \int d\mathbf{x} [n_f^v(\mathbf{x})\mu_{\mathrm{xc}}^{n_f}(\mathbf{x}) - n_1^v(\mathbf{x})\mu_{\mathrm{xc}}^{n_1}(\mathbf{x}) - n_2^v(\mathbf{x})\mu_{\mathrm{xc}}^{n_2}(\mathbf{x})] \; , \tag{2.21}$$

where the superscript v denotes valence only, δE_{xc}^R is given by (2.19), and

$$\delta E_N^v = \sum_{\substack{i \in F_1 \\ j \in F_2}} \frac{Z_i^c Z_j^c}{|\mathbf{R}_i - \mathbf{R}_j|} \tag{2.22}$$

with Z_i^c the core charge of atom i, nuclear location $\mathbf{R}_i$. The evaluation of δE_R thus requires knowledge of the densities and Coulomb potentials of the isolated fragments, the calculation of some overlap integrals involving these quantities, and the determination of the valence eigenvalue sum for the potential $\tilde{V}(\mathbf{x})$ given by (2.12). This is an enormous simplification compared with the problem of minimizing (2.10) directly.

Though the above derivation was carried through for two fragments, the generalization to N fragments is trivial. Equation (2.17) holds without change if the frozen density is

$$n_f(\mathbf{x}) = \sum_{k=1}^{n} n_k(\mathbf{x}) \; ,$$

where the $n_k(\mathbf{x})$ are the individual fragment densities, while the equivalents of (2.18) and (2.21) involve single and pair sums over the fragments. The theory, then, can be applied to intermolecular interactions on a surface as well as to molecule-surface interactions.

III. DISCUSSION OF THE ENERGY EXPRESSION

Though Eq. (2.21) is proposed in connection with complex systems where a direct minimization of the energy functional is prohibitive, I will be concerned in this initial paper with homonuclear dimers. This enables a comparison to be made with essentially exact Kohn-Sham calculations and facilitates a discussion of how (2.21) describes interactions of various types.

The most obvious application of a theory based on frozen overlapped fragment densities is to closed-shell systems and I begin by making contact with the work of Gordon and Kim.[2] For simplicity, I consider He_2, and invoke the local-density approximation for E_{xc},

$$E_{\mathrm{xc}}[n] = \int d\mathbf{x}\, n(\mathbf{x})\epsilon_{\mathrm{xc}}^h(n(\mathbf{x})) \; , \tag{3.1}$$

where $\epsilon_{\mathrm{xc}}^h(n)$ is the exchange-correlation energy of a homogeneous electron gas with density n, for which I take the parametrization of Vosko, Wilk, and Nusair (VWN).[8] This is slightly different from the approximation used by Gordon and Kim, but alters results in no material way. For He_2, internuclear separation R, Eq. (2.18), takes the form

$$\delta E_R = 2\sum_n \delta\tilde{\epsilon}_n + \frac{Z^2}{R} - \int d\mathbf{x}\, n(\mathbf{x}_1)\phi(\mathbf{x}_2) + \int d\mathbf{x} [n_f(\mathbf{x})\Gamma(n_f(\mathbf{x})) - n(\mathbf{x}_1)\Gamma(n(\mathbf{x}_1)) - n(\mathbf{x}_2)\Gamma(n(\mathbf{x}_2))] \; , \tag{3.2}$$

where Z is the nuclear charge, $\mathbf{x}_{1,2}\equiv\mathbf{x}-\mathbf{R}_{1,2}$ with $\mathbf{R}_{1,2}$ the nuclear locations, $n(\mathbf{x})$ and $\phi(\mathbf{x})$ are the atomic density and Coulomb potential, $n_f\equiv n(\mathbf{x}_1)+n(\mathbf{x}_2)$, and

$$\Gamma(n)\equiv\epsilon^{h}_{\mathrm{xc}}(n)-\mu^{h}_{\mathrm{xc}}(n)=-n\frac{d\epsilon^{h}_{\mathrm{xc}}(n)}{dn}\ . \tag{3.3}$$

Equation (3.2) can be cast into a form similar to that of Gordon and Kim by separating out from the eigenvalue sum terms that represent the first-order change in the potential energy due to the overlap of the densities. Recalling that the $\widetilde{\epsilon}_n$ satisfy

$$[-\tfrac{1}{2}\nabla^2+\widetilde{V}(\mathbf{x})-\widetilde{\epsilon}_n]\psi_n(\mathbf{x})=0 \tag{3.4}$$

with

$$\widetilde{V}(\mathbf{x})=\phi(\mathbf{x}_1)+\phi(\mathbf{x}_2)-\frac{Z}{|\mathbf{x}_1|}-\frac{Z}{|\mathbf{x}_2|}+\mu^{h}_{\mathrm{xc}}(n_f(\mathbf{x}))\ , \tag{3.5}$$

we define a sum of "second-order" eigenvalue shifts via

$$\delta T_\epsilon\equiv2\sum_n\delta\widetilde{\epsilon}_n-\int d\mathbf{x}\,n(\mathbf{x}_1)[\widetilde{V}(\mathbf{x})-V_A(\mathbf{x}_1)]-\int d\mathbf{x}\,n(\mathbf{x}_2)[\widetilde{V}(\mathbf{x})-V_A(\mathbf{x}_2)]\ . \tag{3.6}$$

Here $V_A(\mathbf{x})$ is the potential associated with the isolated atom density $n(\mathbf{x})$. Substituting into (3.2) and simplifying, we find

$$\delta E_R=\delta T_\epsilon+\int d\mathbf{x}\,N(\mathbf{x}_1)\Phi(\mathbf{x}_2)+\delta E^{R}_{\mathrm{xc}}\ , \tag{3.7}$$

where

$$\delta E^{R}_{\mathrm{xc}}=\int d\mathbf{x}[n_f(\mathbf{x})\epsilon^{h}_{\mathrm{xc}}(n_f(\mathbf{x}))-n(\mathbf{x}_1)\epsilon^{h}_{\mathrm{xc}}(n(\mathbf{x}_1))-n(\mathbf{x}_2)\epsilon^{h}_{\mathrm{xc}}(n(\mathbf{x}_2))] \tag{3.8}$$

and N and Φ represent the total charge density and Coulomb potential due to nuclei and electrons of the atom. Aside from small differences in the description of exchange and correlation, (3.7) is the same as the Gordon-Kim expression,[2] except that their electron-gas kinetic-energy term

$$\delta T_{\mathrm{GK}}=\tfrac{3}{10}(3\pi^2)^{2/3}\int d\mathbf{x}[n_f^{5/3}(\mathbf{x})-n_a^{5/3}(\mathbf{x}_1)-n_a^{5/3}(\mathbf{x}_2)] \tag{3.9}$$

is replaced by the sum of "second-order" eigenvalue shifts, δT_ϵ. In fact, this sum is almost a true independent-particle kinetic-energy change as can be seen on noting that the integrals on the right-hand side of (3.6) would give the correct potential-energy gain of the independent-electron system defined by (3.4) and (3.5) if the dimer density were exactly equal to n_f. Equation (3.7) is thus a derivation of the Gordon-Kim energy formula if (3.9) is understood to represent an approximation for δT_ϵ.

The comparison can be carried further if we evaluate the eigenvalue sum explicitly by solving (3.4) approximately in a linear combination of atomic orbitals (LCAO) basis. For He$_2$ we can expect a good approximation to result from the ansatz for the eigenfunctions,

$$\psi_\pm(\mathbf{x})=\frac{1}{\sqrt{2(1\pm S)}}[\psi_a(\mathbf{x}_1)\pm\psi_a(\mathbf{x}_2)]\ , \tag{3.10}$$

where

$$S=\int d\mathbf{x}\,\psi_a(\mathbf{x}_1)\psi_a(\mathbf{x}_2) \tag{3.11}$$

is the overlap integral and

$$\psi_a(\mathbf{x})=\frac{1}{\sqrt{2}}n^{1/2}(\mathbf{x}) \tag{3.12}$$

is the helium 1s function, for which I take the Clementi form used by Gordon and Kim [strictly, $\psi_a(x)$ should solve (3.4) with $\widetilde{V}(\mathbf{x})$ replaced by $V_A(\mathbf{x})$, the local-density atomic potential]. The plus and minus signs in (3.10) refer to the bonding and antibonding dimer levels both of which are fully occupied. With the solution of the independent-electron problem (3.4) in the basis (3.10), it is easy to show that to lowest order in S,

$$\delta T_\epsilon=-2S\int d\mathbf{x}\,\psi_a(\mathbf{x}_1)[2\widetilde{V}(\mathbf{x})-V_A(\mathbf{x}_1)-V_A(\mathbf{x}_2)]\psi_a(\mathbf{x}_2)\ , \tag{3.13}$$

an expression that bears little resemblance to the Thomas-Fermi kinetic energy δT_{GK}, given by (3.9). Nevertheless, both expressions have a similar magnitude for He$_2$ as can be seen in the inset of Fig. 1, where $\ln(\Delta T_{\mathrm{GK}})$ and $\ln(\Delta T_\epsilon)$ are plotted against internuclear separation R. Other workers have pointed out the accuracy with which the Thomas-Fermi formula reproduces the kinetic energy (KE) associated with atomic densities.[9] Here we note that the same appears to be true for the difference KE when two closed-shell densities overlap.

The energy curves that result from (3.7) with the first term given by (3.13) (solid line) and (3.9) (dashed line), respectively, are shown in Fig. 1 together with a CI calculation (dashed-dotted line) that is believed to be converged on the scale of the figure.[10] This curve is reproduced rather well if one combines the exact Hartree-Fock repulsion with the asymptotic van der Waals attraction. The energy curve resulting from the present theory shows the strongest attraction and is similar to the fully self-consistent Kohn-Sham local density (KS-LDA) calculation of Jones.[11] The difference is essentially a displacement of Jones's curve inwards by $\simeq0.1$ a.u. and is due in part to the use of an atomic density which is more compact than the KS-LDA density. Figure 1 demonstrates the accuracy of (3.7) as an approximation to a full KS-LDA calculation but shows also that, whether used for exchange and correlation alone or, in addition, for the free-particle kinetic energy, the local-density approximation fails rather badly for He$_2$. This is not really surprising since the approximation is known to give incorrect results in the outer regions of atoms where the exchange-correlation hole radius ceases to bear any relation to the local density. However, it is useful to explore the form of the curves in Fig. 1 a little more closely in order to pin down more precisely where the error lies.

Of the three terms in Eq. (3.7), the second will appear in all theories (if not explicitly). In fact, this term, of order S^2, is rather small ($\simeq-1$ meV at $R=5$ a.u.), and the energy balance for He$_2$ is determined primarily by the

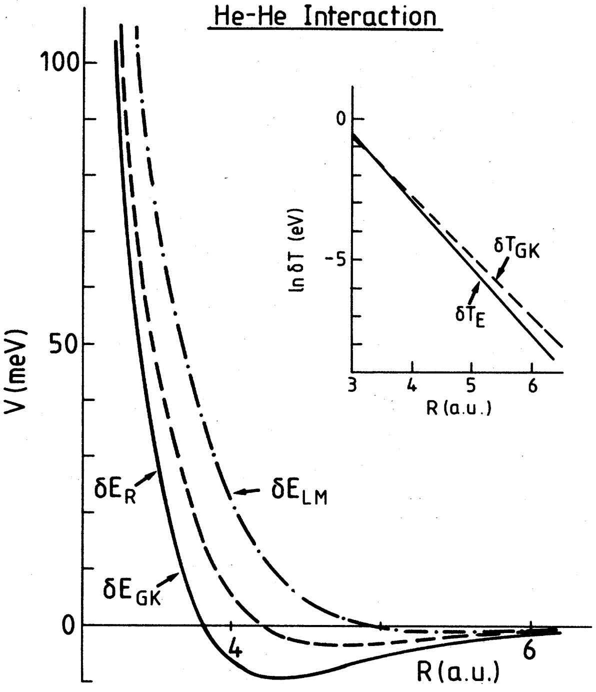

FIG. 1. Helium-helium interaction as given by Eq. (3.7) with the eigenvalue sum approximated by δT_ϵ (solid line marked δE_R), and by δT_{GK} (dashed line marked δE_{GK}). The dashed-dotted line gives the CI result of Liu and McLean (Ref. 10). The inset shows a comparison of δT_ϵ and δT_{GK} on a log scale.

competition between exchange-correlation attraction and kinetic-energy repulsion. In a Hartree-Fock description the exchange attraction and the kinetic repulsion have essentially the same range, both being roughly proportional to S^2. Since the kinetic term is larger than the sum of direct-Coulomb and exchange terms, the Hartree-Fock energy curve is monotonic in R and repulsive and the net interaction becomes attractive at large distance only because of the van der Waals contribution, which is a pure correlation energy and falls off like R^{-6} at large distances. Since the overlap S falls off exponentially, the van der Waals interaction is zeroth order in S and the exact curve in Fig. 1 can be written schematically in the form

$$\delta E_{\text{LM}} \simeq (C_T^{\text{HF}} - C_x^{\text{HF}}) S^2 - C_6 / R^6 \,. \tag{3.14}$$

Consider now Eq. (3.7). The eigenvalue sum, δT_ϵ in (3.13), falls off like S^2 as in Hartree-Fock, but the exchange-correlation term does not. In an exchange-only approximation, for instance, $\epsilon_{\text{xc}}^h(n)$ is strictly proportional to $n^{1/3}$. Since this is the dominant dependence, (3.7) behaves roughly as

$$\delta E_R \simeq C_T S^2 - C_{\text{xc}} S^{4/3} \,, \tag{3.15}$$

and the balance between kinetic repulsion and exchange attraction is different from that in (3.14). Equation (3.15) shows that the LDA predicts attraction between all systems at large separation mainly because it assigns an unphysically long range to exchange interactions and not because, in any sense, it simulates van der Waals interactions. In fact, KS-LDA theory consistently overestimates the exchange-correlation energy gain due to the weak overlap of density distributions, and net interactions between inert atoms are better given by the Gordon-Kim approximation, which, however, improves the situation not by remedying the defect of the LDA for exchange and correlation, but by matching the mistake with another. Their approximation (3.9) gives a kinetic energy that falls off not like S^2, but roughly like $S^{5/3}$ (see the inset of Fig. 1). Thus

$$\delta E_{\text{GK}} \simeq C_T^{\text{GK}} S^{5/3} - C_{\text{xc}}^{\text{GK}} S^{4/3} \,, \tag{3.16}$$

and the KE repulsion as well as the exchange attraction has too long a range. It is curious and presumably not without significance that a theory which partially cancels one mistaken distance dependence against another nevertheless gives a remarkably respectable picture of the mutual interactions of many inert atoms and ions.

Whereas Gordon and Kim restricted themselves to inert systems, Eq. (3.7) is valid generally within the framework of Kohn-Sham theory. The hallmark of a covalent bond, for instance, is the appearance of a term in δT_ϵ that is asymptotically proportional to S and attractive. For example, if we were to occupy only bonding orbitals in (3.10), simulating the H_2 molecule rather than the He_2 dimer, then the eigenvalue sum is given, again to lowest order in S, not by (3.13), but by

$$\delta T_\epsilon \simeq \int d\mathbf{x}\, \psi_a(\mathbf{x}_1)[2\tilde{V}(\mathbf{x}) - V_A(\mathbf{x}_1) - V_A(\mathbf{x}_2)]\psi_a(\mathbf{x}_2) \,, \tag{3.17}$$

which is negative definite. The balance of the three terms in (3.7), all of which are now attractive at large separations, is then radically altered, and δE_ϵ forms a minimum only because the electrostatic term becomes strongly positive as the overlap increases and the internuclear repulsion dominates.

A third type of chemical bond arises as a result of the incorporation into the coupled fragment ground state of levels unoccupied in the isolated fragments. Returning to the case of closed shells that I described earlier using the LCAO ansatz (3.10), suppose that we now calculate the second-order eigenvalue shift using an extended basis that includes unoccupied p_z-like atomic functions. That is, we supplement (3.10) with additional functions

$$\psi_\pm^p(\mathbf{x}) = \frac{1}{[2(1 \mp S_p)]^{1/2}} [\psi_a^p(\mathbf{x}_1) \mp \psi_a^p(\mathbf{x}_2)] \,, \tag{3.18}$$

where $\psi_a^p(\mathbf{x})$, like $\psi_a(\mathbf{x})$, solves (3.4) with $\tilde{V}(\mathbf{x}) = V_A(\mathbf{x})$. Let ϵ_s, ϵ_p be the atomic eigenvalues corresponding to the s- and p-atomic functions and assume for simplicity that $\epsilon_p - \epsilon_s$ is large compared with the bonding-antibonding splittings that arise. Solving (3.4) for internuclear potential $\tilde{V}(\mathbf{x})$ in the extended basis [Eqs. (3.10) and (3.18)], we obtain two sets of bonding and antibonding orbitals; the lower-lying of which is predominantly s with a small admixture of p, the higher-lying being predominantly p with a small admixture of s. For a closed-shell atomic configuration, the lower set of levels is completely filled, the upper set empty. On evaluating the second-order eigenvalue sum, we then find to lowest order in S

$$\delta T_\epsilon \simeq -2SV_s - \frac{4(V_{12}^2+V_{11}^2)}{(\epsilon_p-\epsilon_s)} , \tag{3.19}$$

where V_s is the matrix element in (3.13) and V_{12} and V_{11} are given by

$$V_{12} \equiv \int d\mathbf{x}\, \psi_a(\mathbf{x}_1)[\widetilde{V}(\mathbf{x})-V_a(\mathbf{x}_1)]\psi_a^p(\mathbf{x}_2) \tag{3.20}$$

and

$$V_{11} \equiv \int d\mathbf{x}\, \psi_a(\mathbf{x}_1)[\widetilde{V}(\mathbf{x})-V_a(\mathbf{x}_1)]\psi_a^p(\mathbf{x}_1) . \tag{3.21}$$

The first term in (3.19) is the closed-shell repulsion found earlier, on which is superimposed an attractive polarization contribution whose magnitude depends on the matrix elements (3.20) and the energy separation of the atomic eigenvalues. The physical origin of the polarization term is, of course, well known. The closed-shell repulsion arises because the Pauli principle inhibits the hopping of an electron from one site to another. The presence of an unfilled level allows an electron on one site to make an indirect hop and enjoy the Coulomb attraction of the other site without paying the price exacted by the exclusion principle.

Although the existence of polarization interactions has been known since quantum chemistry began, their influence on bonding characteristics has apparently been underestimated until very recently. For example, Trenary *et al.* were surprised to find a Hartree-Fock bond energy for the complex $AlOH_2$ of $\simeq$0.2 eV, referring to a hitherto unsuspected interaction.[12] This is a clear case of a polarization interaction involving donation to unfilled Al ($3p$) levels. Similarly, interactions amongst group-IIA atoms were thought to be analogous to those between rare-gas atoms until KS-LDA calculations showed otherwise.[11] Equation (3.20) indicates that the size of the polarization contribution depends sensitively on the separation of filled and unfilled levels in the atom, and so is an analytic confirmation of Jones's interpretation of binding-energy trends down to the group-IIA row.[11] One of the areas where the present simplified calculational scheme is likely to prove useful concerns interactions between strongly-bound molecules such as H_2O and NH_3 and metal surfaces. These molecules are all weakly bound by polarization forces with minimal changes in the density, and their interactions should be given no less accurately by (2.12), or equivalently (3.7), than by fully self-consistent Kohn-Sham calculations.

As a final example I consider the relation between the present approach and the eigenvalue formula of Zaremba and Kohn for the interaction between a helium atom and a metal surface.[13] This formula, derived strictly within Hartree-Fock, relates the asymptotic repulsion directly to a sum of eigenvalue shifts with the corrections evident in (2.18) or (2.21) absent. In fact, one can derive the equivalents of these equations in Hartree-Fock and the exchange-correlation terms do indeed cancel, as I now indicate. The $1s$ orbital of helium lies well below the bottom of the metal band, and therefore in the present context can be regarded as a core orbital. The relevant equation is thus (2.21), where the valence sum refers solely to the metal functions and eigenvalues. Since the exchange term in Hartree-Fock involves the orbitals directly, we must work with frozen orbitals rather than frozen densities. It is then easy to show that Eq. (2.21) holds with quadratic errors within Hartree-Fock, provided we reinterpret the exchange-correlation terms appropriately. For example, the potential $\widetilde{V}(\mathbf{x})$ in (2.21) has a nonlocal exchange term in place of $\mu_{xc}^{n_f}(\mathbf{x})$, whose operation on an arbitrary one-electron orbital $\phi(\mathbf{x})$ is given by

$$\begin{aligned}\hat{\mu}_x^f(\mathbf{x})\phi &= -\int d\mathbf{x}' \sum_{\mathbf{k}} \frac{\psi_k^*(\mathbf{x})\psi_k(\mathbf{x}')\phi(x')}{|\mathbf{x}-\mathbf{x}'|} \\ &\quad -\int dx' \frac{\psi_a(\mathbf{x})\psi_a(\mathbf{x}')\phi(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \\ &\equiv (\hat{\mu}_x^m+\hat{\mu}_x^a)\phi ,\end{aligned} \tag{3.22}$$

where $\psi_{\mathbf{k}}$, ψ_a are the frozen orbitals of the metal and helium atom. Since the atom has no valence orbitals, the final term in (2.21) then takes the form

$$\begin{aligned}&-2\sum_{\mathbf{k}} (\langle \mathbf{k}|\hat{\mu}_x^m+\hat{\mu}_x^a|\mathbf{k}\rangle - \langle \mathbf{k}|\hat{\mu}_x^m|\mathbf{k}\rangle) \\ &\qquad\qquad \equiv -2\sum_{\mathbf{k}} \langle \mathbf{k}|\hat{\mu}_x^a|\mathbf{k}\rangle ,\end{aligned} \tag{3.23}$$

while the penultimate term, a pure exchange energy difference is

$$\begin{aligned}\delta E_x^R &= \sum_{\mathbf{k}} \langle \mathbf{k}|\hat{\mu}_x^a|\mathbf{k}\rangle + \langle a|\hat{\mu}_x^m|a\rangle \\ &= 2\sum_{\mathbf{k}} \langle \mathbf{k}|\hat{\mu}_x^a|\mathbf{k}\rangle .\end{aligned} \tag{3.24}$$

These two terms therefore cancel exactly and, noting that the direct electrostatic repulsion is zero because the helium $1s$ electrons have been treated as core, we obtain the Zaremba-Kohn result

$$\delta E_R^{\mathrm{HF}} = 2\sum_{\mathbf{k}} \delta\epsilon_{\mathbf{k}}^{\mathrm{HF}} , \tag{3.25}$$

where $\delta\epsilon_{\mathbf{k}}^{\mathrm{HF}}$ are the shifts in the band eigenvalues that result from the scattering of the metal electrons from the Hartree-Fock potential of the helium atom.

Interestingly, the exact cancellation of terms that leads to (3.25) is a unique feature of Hartree-Fock and results from the simple relation (3.24) between exchange energy of interaction, ΔE_x^R, and the exchange potential. Other theories of exchange and correlation, e.g., local-density approximations, show only a partial cancellation, and the correlation terms in (2.21) must then be included explicitly. The local-density approximation has been proposed in connection with the helium-metal interaction,[14] and I note only the objection raised earlier with respect to He_2, that the attractive tail of the LDA interaction arises because an unphysical range has been ascribed to exchange interactions and not because, e.g., the LDA simulates van der Waals interactions or describes the effect of overlap of charge clouds on the correlation energy.

TABLE I. Spectroscopic constants of homonuclear dimers. E_b is the well depth, R_e the equilibrium separation, and ω_e the vibration frequency. Experimental values from Ref. 16, for Be_2 from Ref. 17. Column marked PA gives the KS-LDA-VWN results of Painter and Averill (Ref. 18).

	E_b (eV)			R_e (a.u.)			ω_e (meV)		
Dimer	(2.21)	PA	Expt.	(2.21)	PA	Expt.	(2.21)	PA	Expt.
Be_2	0.49	0.50	~0.1	4.50	4.63	4.66	45	45	28
C_2 $({}^1\Sigma_g^+)$	8.7	7.19	6.2	2.20	2.36	2.35	246	232	230
N_2	10.7	11.34	9.91	2.03	2.08	2.07	346	296	292
F_2	3.7	3.32	1.65	2.71	2.62	2.68	120	133	111
Cu_2	2.9	2.65	2.03	4.10	4.10	4.20	35	41	33

IV. EXPLICIT CALCULATIONS FOR DIMERS

The results of the preceding section illustrate in a qualitative way how the energy formula (2.21) describes bonding of various types. In this section I quote specific results for a few dimers to illustrate the level of accuracy that can be expected in practical applications. The local-density approximation for exchange and correlation, Eq. (3.1), will be used throughout. For convenience, I reproduce Eq. (2.21) again, assuming the LDA and a homonuclear dimer. The nuclei are located at $\mathbf{R}_1,\mathbf{R}_2$, with $R=|\mathbf{R}_1-\mathbf{R}_2|$, and the coordinates of a given point $\mathbf{x}$ with respect to $\mathbf{R}_1,\mathbf{R}_2$ are denoted $\mathbf{x}_1,\mathbf{x}_2$. The bond energy at separation R is then

$$\delta E_R=\delta E_{\text{eig}}+\delta E_{\text{es}}+\delta\Gamma_{\text{xc}}\ , \tag{4.1}$$

where

$$\delta E_{\text{eig}}=\sum_n^v a_n\delta\epsilon_n\ , \tag{4.2}$$

$$\delta E_{\text{es}}=\frac{Z_c^2}{R}-\int d\mathbf{x}\, n^v(\mathbf{x}_1)\phi^v(\mathbf{x}_2) \tag{4.3}$$

and

$$\begin{aligned}\delta\Gamma_{\text{xc}}=\int d\mathbf{x}\{&[n_f(\mathbf{x})\epsilon_{\text{xc}}^h(n_f(\mathbf{x}))-n(\mathbf{x}_1)\epsilon_{\text{xc}}^h(n(\mathbf{x}_1))-n(\mathbf{x}_2)\epsilon_{\text{xc}}^h(n(\mathbf{x}_2))]\\&-[n_f^v(\mathbf{x})\mu_{\text{xc}}^h(n_f(\mathbf{x}))-n^v(\mathbf{x}_1)\mu_{\text{xc}}^h(n(\mathbf{x}_1))-n^v(\mathbf{x}_2)\mu_{\text{xc}}^h(n(\mathbf{x}_2))]\}\ ,\end{aligned} \tag{4.4}$$

with Z_c the core charge, $n(\mathbf{x})$ the isolated atom density, $n^v(\mathbf{x})$ that part due only to valence electrons, $\phi^v(\mathbf{x})$ the valence Coulomb potential, and $n_f(\mathbf{x})=n(\mathbf{x}_1)+n(\mathbf{x}_2)$. The atomic densities, eigenvalues, and Coulomb potential were generated numerically in an atom program, and the integrals needed to evaluate δE_{es} and $\delta\Gamma_{\text{xc}}$ were calculated by interpolation onto an elliptic coordinate mesh and straightforward Gaussian quadrature. This gave sufficient accuracy for present purposes, though a more careful treatment of the electrostatic energy is necessary for very weakly interacting systems.[2]

The only nontrivial computational step is the determination of the eigenvalue sum in (4.1). An important property of this sum is that it obeys a variational principle (being merely the total energy of independent electrons in a fixed potential), so that a precise determination of each eigenvalue is unnecessary. Variation was carried out by solving a standard LCAO problem using a partial-wave basis of localized muffin-tin orbitals that was described previously in connection with full KS-LDA calculations for clusters.[15] *s*, *p*, and *d* waves were included in all cases. The orbitals are determined by the potential and by tail parameters that are varied sequentially. The overlap of core densities was treated by the expedient of folding back the core tails and renormalizing to a fixed radius R_c.[15] The energy can then be calculated within the frozen core approximation for $R\geq 2R_c$ and the dimer eigenvalues converge at large R to values shifted slightly from the exact atomic eigenvalues. The asymptotic limit was determined by solving an atomic eigenvalue problem using the renormalized core. Since the effect was rather small even for the strongly-bonded dimers, a more complete treatment of the core was not considered worthwhile.

Spin polarization is not trivially included in the present formalism, because the spin density depends primarily on the configuration and is usually very different in dimer and constituent atoms so that there is no obvious reference spin density about which to expand. A perturbative treatment is possible, but would require some estimate of the spin density in the dimer. In this paper I consider only singlet dimer states. Equation (4.1) then gives the binding energy of the dimer with respect to the non-spin-polarized atoms. The energy lowering in the atoms due to the presence of parallel spins is calculated separately and subtracted off to give a net binding energy that can be compared consistently with the results of full Kohn-Sham local-spin-density approximation (LSDA) calculations.

This comparison is shown in Table I for five dimers having different bonding properties and giving rise to a wide range of difference densities, $\delta n(\mathbf{x})$ [Eq. (2.11)]. The fundamental spectroscopic parameters, well depth E_b, equilibrium separation R_e, and vibration frequency ω_e,

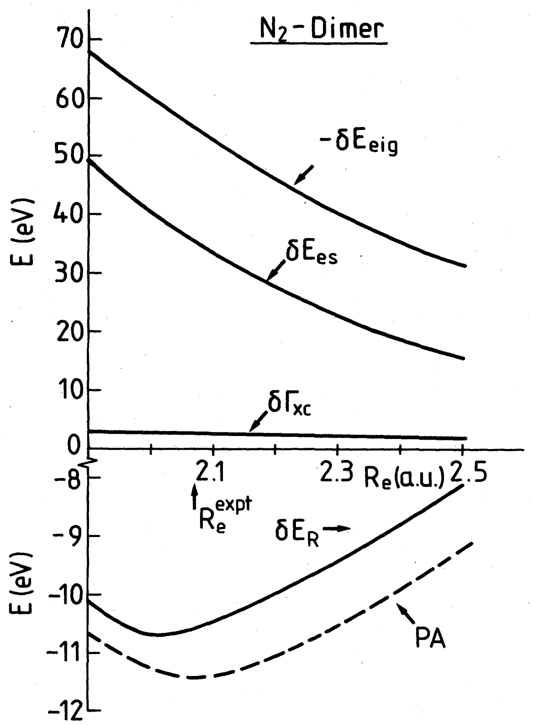

FIG. 2. Binding energy curve of N_2 molecule. Solid line, Eq. (4.1); dashed line, full KS-LDA result (Ref. 18). The three components in Eq. (4.1) are plotted separately in the upper part of the figure. The arrow denotes the experimental equilibrium separation (Ref. 16).

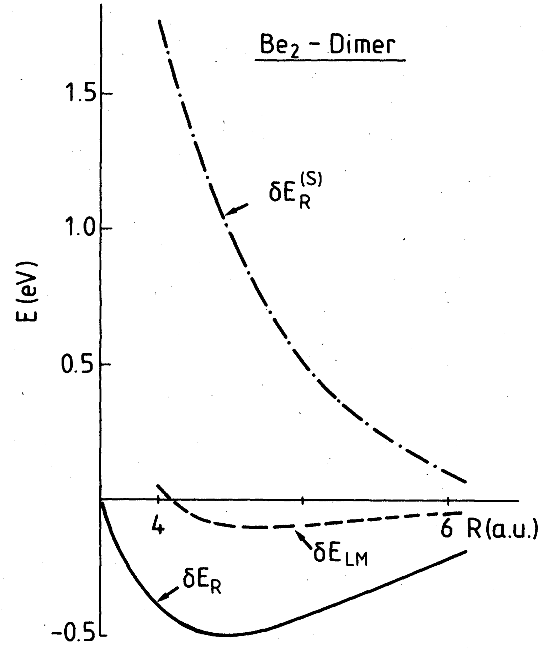

FIG. 3. Binding energy curve of Be_2 dimer. δE_R from Eq. (4.1); $\delta E_R^{(s)}$, same, but eigenvalue sum calculated using only s waves in the orbital basis. δE_{LM} is a CI calculation (Ref. 21). The figure illustrates the strong influence of the Be $(2p)$ shell on the energy curve.

are shown as given by Eq. (2.21) (first column), by fully self-consistent LSDA calculations using the same functional for exchange and correlation (second column)[18] and by analysis of band spectroscopic data.[16,17] The experimental results are included for purposes of orientation and the significant comparison is between the two sets of calculationed parameters. Aside from small discrepancies that may arise because of orbital basis error, or use of frozen-core approximation in the present work, the differences between the calculations are a direct measure of the accuracy of the energy expression (2.21). As can be seen, the approximation is excellent for Be_2, where the closed-shell configuration ensures that the density difference $\delta n(\mathbf{x})$ is small, and is rather respectable even for very strong covalent bonds. The worst case is the doubly π-bonded ground state of C_2, which has an extended electron density rather different from the sum of overlapped atom densities. Even for this dimer, however, the bond distance and vibration frequency are in error by only $\simeq 6\%$. As with the full KS-LDA calculations, the most erratic quantity is the absolute binding energy which is too large for C_2, F_2, and Cu_2 and too small for N_2, a behavior which seems to correlate with the sign of the difference density $\delta n(\mathbf{x})$ at the bond center.[19] An analysis of the error requires carrying the expansion to higher order in δn, which is nontrivial because some quadratic terms involve coupling to excited states [cf. Eq. (2.14)] and there are positive and negative contributions. The essential idea of this paper—to give a method of calculating the energy approximately without determining the molecular density and Coulomb potential—would in any event have to be abandoned if the expansion in δn is carried to higher order. If the level of accuracy shown in Table I is insufficient, a full calculation would have to be performed.

Figure 2 shows a comparison of the N_2 ground-state energy curve with the result of Painter and Averill.[18] The difference between the two curves near the minimum is due in the main to the electrostatics and illustrates that the nuclear descreening responsible for the upturn of the energy curve is not described correctly by Eq. (4.1). It is interesting to compare the individual terms in (4.1) with their equivalents in a full KS-LDA calculation,[19] involving the sum of eigenvalues of the self-consistent potential and an electrostatic term in which the true molecular density appears. Both are substantially smaller in magnitude than the corresponding terms in (4.1). The electrostatic repulsion is smaller because the bonding charge screens the nuclei better than the sum of overlapped atom densities. The sum of self-consistent eigenvalues is smaller because the eigenfunctions of a fixed potential can accumulate bonding charge without penalty. Iteration towards self-consistency using the fixed potential as a starting point would raise the potential at the bond center, expelling charge from the bond region and raising the eigenvalues of bonding orbitals until equilibrium is attained.

Equation (4.1) does not describe these two effects independently, but trades one off against the other to lowest order in the difference density. The three terms $\delta E_{\rm eig}$, $\delta E_{\rm es}$, and $\delta\Gamma_{\rm xc}$ are shown separately in Fig. 2, where the strong competition between the first two contributions is evident. This behavior is typical for all the dimers. Note that (4.1) and the Gordon-Kim form (3.7) are equivalent. As is clear from the discussion in Sec. III, the latter is a more physically appealing way of separating the energy into different components, though the former is calculationally more convenient.

In concluding this section I make some remarks concerning the energy curve of Be_2, which until recently was regarded as very weakly bound with an equilibrium separation $\simeq 8$ a.u.[20] Figure 3 shows three calculations of the energy curve. The solid line is the present result and is practically identical with that obtained by Painter and Averill.[18] The dashed curve is a recent CI calculation[21] that gives spectroscopic parameters in good agreement with experiment. Though the KS-LDA calculation was the first to show a substantial bond energy and gives a good value for the equilibrium separation, the large error in E_b is alarming and points to a serious flaw in the LDA for such systems. To set this error in perspective I show as the dashed-dotted curve in Fig. 3 a calculation within the present scheme, but with an orbital basis that includes only s functions. The difference between this and the solid curve measures the polarization effect discussed in Sec. III [cf. the final term in Eq. (3.19)] that is responsible for the binding. If the LDA error in E_b is now viewed as a fraction of the polarization contribution, it seems considerably less alarming, especially since the LDA underestimates the s-p promotion energy for the Be atom by 0.2 eV.[11] However, the population of the p orbitals in the Be_2 bond is only a small fraction of an electron, so that the promotion error is unlikely to be the only source of the overbinding. In fact, it is probable that much of the error is already present in the dashed-dotted curve, which gives the energy of a truly closed-shell heliumlike system. As mentioned earlier, the LDA ascribes an unphysical range to exchange interactions for such systems with the result that the energy curve does not rise steeply enough. This was borne out by a calculation using the Hartree-Fock version of the present theory and an s-orbital-only basis, which gave an energy curve substantially more repulsive than the dashed-dotted line in Fig. 3. These observations suggest that an improvement over LDA with respect to fragments that are weakly bound by polarization forces would require as an integral feature a more accurate description of closed-shell repulsion. As a final remark in this context I note that a rough estimate of the Langreth-Mehl[22] correction to the LDA raised the energy curve by about 0.15 eV at minimum. This correction therefore represents an important, though not decisive, improvement.

Although the applications in this section refer to dimers where charge transfer is prohibited, some similar calculations for heteronuclear diatomics show that the occurrence of moderate charge shifts does not obviate the approximation. Where very large charge shifts are encountered, however, there is a marked tendency towards a too low binding energy. This is because of the positive definite, quadratic term $\frac{1}{2}\int d\mathbf{x}\,\delta n(\mathbf{x})\delta\phi(\mathbf{x})$ that was neglected in deriving (2.17) and is only partially compensated by the negative corrections in (2.14).

V. SUMMARY

A method has been presented for the approximate evaluation of the interaction energy of fragments within the Kohn-Sham scheme that does not require a determination of the electron density and Coulomb potential of the coupled system. The method is an extension of the Gordon-Kim approach beyond inert atom interactions. However, the approximate energy expression is not postulated, but arrived at by expanding the Kohn-Sham energy about a reference density, normally the sum of overlapped frozen fragment densities, and a reference potential constructed from this density. The only nontrivial step in determining the energy is the variational evaluation of an eigenvalue sum for an independent-electron Hamiltonian with the potential term given by the reference potential. The error with respect to the exact Kohn-Sham energy may be positive or negative and will be small to the extent that the actual density of the coupled fragments resembles the reference density. Explicit calculations for dimers show a negligible error for closed-shell or quasi-closed-shell dimers such as Be_2. For covalently-bonded dimers the error is larger but still sufficiently small to yield useful results in systems where a complete solution of the Kohn-Sham problem is not feasible. The method is not limited to a particular approximation for exchange and correlation, and its inherent simplicity may assist the search for improvements to the local-density approximation. Applications under consideration include interactions between molecules and between a molecule and a surface.

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