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(NASA-CR-164035) QUANTUM CHEMICAL
CALCULATION OF THE EQUILIBRIUM STRUCTURES OF
SMALL METAL ATOM CLUSTERS Annual Progress
Report, 1 Apr. 1980 - 29 Feb. 1981 (Battelle
Columbus Labs., Ohio.) 78 p HC A05/MF A01

N81-19881

Unclass
41696

G3/72

Report



ANNUAL PROGRESS REPORT

on

QUANTUM CHEMICAL CALCULATION OF THE EQUILIBRIUM
STRUCTURES OF SMALL METAL ATOM CLUSTERS

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
AMES RESEARCH CENTER

March 27, 1981

by

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Grant NSG-2027

This covers the Period April 1, 1980 to February 29, 1981

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I. INTRODUCTION

The goal of this research is to gain quantitative fundamental understanding of the properties and behavior of clusters of metal atoms as a function of the number of atoms in the cluster. Among the properties of interest are the various possible equilibrium structures a cluster of atoms may adopt as each atom is added, the relative stability and degree of order of these equilibrium structures, their characteristic fundamental modes of vibration, and the magnitude of the energy barriers regulating the rate of interconversion of one equilibrium cluster structure to another one.

II. SCIENTIFIC PROGRESS

During this reporting period, scientific progress was made in two different areas. Continuing progress was made on developing the capability to calculate gradients of the matrix elements of the effective core potential. Particular emphasis has been given towards finding a suitable algorithm for the efficient processing of the derivative integrals after use has been made of the combined translational and rotational invariance properties of the integrals to reduce the integral calculation to just the truly linearly independent derivative integrals.

The most significant progress during this period, however, consists of the development of an entirely new approach to the calculation of electronic potential energy surfaces. The details of this new approach are

described in Appendix A in the form of a preprint of a manuscript that has been submitted for publication to The Journal of Chemical Physics. This new approach is based upon the atom-superposition-and-electron-delocalization (ASED) model of chemical binding. It has the advantage of dividing the electronic energy into physically transparent groups of terms. Moreover, whereas conventional methods approach a molecular calculation without recourse to the information already calculated from the component atoms, the structure of the ASED energy lends itself to the fullest utilization of the properties already available about the atomic solution in order to simplify the calculation of the molecular energy. This new approach has prospects of reducing even by an order of magnitude the effort required in the calculation of the molecular energy, and thereby constitutes a major step towards accomplishing the goals of this research explained in the introduction.

APPENDIX A

A new approach to the calculation of potential
energy surfaces

A first-principles analog of the semi-empirical atom-superposition-
and-electron-delocalization method for calculating potential
energy surfaces

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ABSTRACT

A new decomposition of the molecular energy is presented that is motivated by the atom-superposition-and-electron-delocalization physical model of chemical binding. The energy appears in physically transparent form consisting of a classical electrostatic interaction, a zero-order two-electron exchange interaction, a relaxation energy, and the atomic energies. Detailed formulae are derived in zero- and first-order of approximation. The formulation extends beyond first order to any chosen level of approximation leading, in principle, to the exact energy. The structure of this energy decomposition lends itself to the fullest utilization of the solutions to the atomic sub-problems to simplify the calculation of the molecular energy. If non-linear relaxation effects remain minor, the molecular energy calculation requires at most the calculation

of two-center two-electron integrals. This scheme thus affords the prospects of substantially reducing the computational effort required for the calculation of molecular energies.

I. INTRODUCTION

In molecular problems involving large numbers of electrons, as in the case of molecules consisting of many transition-metal atoms and many carbonyl groups, the application of the standard first-principles methods of molecular quantum mechanics^(1,2) becomes impracticable. In these cases one must resort to more approximate methods^(3,4) that, while practical, retain the prospects of yielding a realistic physical description of chemical binding.

One semi-empirical method that has been actively applied to large electronic-structure problems is the atom-superposition-and-electron-delocalization (ASED) method of Anderson⁽⁵⁾. This method has the desirable property that, in addition to the molecular one-electron energy levels, it also yields an approximate molecular total energy as a function of the function of the positions of the constituent atoms. The application of this method to large molecules has been shown to yield useful predictions of molecular structure, force-constants, and relative bond strengths⁽⁶⁻¹⁰⁾. The application of the ASED method ranges from the study of the structures of clusters of transition-metal atoms⁽⁷⁾, to the study of molecules chemisorbed on metal-cluster surfaces⁽⁸⁾, to the study of organometallic complexes^(9,10).

The ASED method is a semi-empirical method. The molecular orbital energies are obtained by what is in essence the extended-Hückel method^(5,11). The ASED molecular energy *ansatz* is obtained by combining an energy that is derived from an approximation to the integral Hellmann-Feynman force formula^(5,12) with the sum of molecular orbital energies (the extended-Hückel energy).

The validity of the ASED method rests mainly on the evidence provided by the numerous useful applications that have resulted from its use. There exists, however, no first-principles derivation of the ASED method that would show how this method fits as a particular step into a well-defined hierarchy of approximations to the exact molecular energy. The absence of such a theoretical basis has been the source of skepticism about the validity of the ASED method. Recently, Anderson has presented work aimed at elucidating the theoretical basis of the ASED method.⁽¹³⁾ While the physical reasoning in this work, based on a time-dependent approach to chemical bonding, is compelling, the formulation of the analytical aspects of the method, especially for the many-electron cases, remain heuristic.

In this paper we present a first-principles decomposition scheme of the molecular total energy using the conventional procedures of molecular quantum mechanics. We have attempted to adhere, as closely as we found possible, to the ASED physical model of the stages in the bonding process to set up the basic steps from which then flow, as a consequence, the definitions of the terms in the decomposition of the energy. This energy decomposition is formulated so that it may, in principle, be taken to any chosen level of approximation leading up to the exact energy. There are some inherent differences in a semi-empirical approach and a first-principles approach such as the present one. Without attempting to resolve this issue, we find that in zero-order of approximation the present energy decomposition does indeed have an analogy in the form of its terms to the semi-empirical ASED energy *ansatz*. This analogy in form, however, does not extend beyond the zero-order level. The inclusion of the first-order

correction terms yields a different energy formula that, nevertheless, corresponds physically even more closely to one of the main effects envisioned in the ASED physical picture of the chemical bonding process, namely the relaxation effects subsequent to the rigid-atom superposition stage. The main themes of the ASED physical model of chemical bonding are found to reemerge in generalized form even on including higher order corrections to the energy decomposition.

II. THE ASED SEMI-EMPIRICAL METHOD

Procedurally, the ASED method consists of two steps. The first step is the calculation of pair-wise interaction energies among the atoms in the molecule using the formula

$$E_R = \sum_{A > B} \sum \left[Z_B \left(\frac{Z_A}{\| \underline{R}_A - \underline{R}_B \|} - \int \frac{\rho_A^{\text{at}}(\underline{r} - \underline{R}_A)}{\| \underline{r} - \underline{R}_B \|} d\underline{r} \right) \right] \quad (1)$$

The summations range over all unique pairs of atom labels A and B, and the symbols \underline{R}_A , Z_A , and $\rho_A^{\text{at}}(\underline{r} - \underline{R}_A)$, for example, refer to the position vector, nuclear charge, and atomic charge density of the A'th atom respectively. The spatial coordinate vector is written as \underline{r} . The second step is the calculation of the molecular orbital energies, $\{\epsilon_k, k = 1, \dots, n\}$, by solving the secular equation

$$\sum_A \sum_{\mu \in S_A} \left(H_{\mu, A; \nu, B} - \epsilon_k S_{\mu, A; \nu, B} \right) C_{\mu, A; k} = 0$$

$$\nu \in S_B; \quad k = 1, \dots, n \leq N \quad (2)$$

The restrictions and approximations to this equation are the same as in the extended Hückel method.⁽¹¹⁾ The basis set on each atom, S_A , is

restricted to a minimal set of valence atomic orbitals. The $S_{\mu,A;\nu,B}$'s are the elements of the overlap matrix. The hamiltonian matrix elements are defined as

$$H_{\mu,A;\nu,A} \equiv - I_{\mu,A} \delta_{\mu,\nu} \quad (3a)$$

$$H_{\mu,A;\nu,B} \equiv - \frac{1}{2} K \left(I_{\mu,A} + I_{\nu,B} \right) S_{\mu,A;\nu,B} \quad (3b)$$

The $I_{\mu,A}$ is the ionization potential for removal of an electron from the μ 'th orbital of the A'th atom. The K factor, based on experience with first-row diatomic molecules, is defined by Anderson⁽⁵⁾ as

$$K = 2.25 e^{-0.13D} \quad (4)$$

where D is the distance between the centers. Note that we shall be using Hartree atomic units in all the equations. When required, the following conversion factors are used: 1 bohr = 0.529177Å, 1 hartree = 27.21165 e.V. The approximate total energy of the ASED method is obtained by combining the extended Hückel energy⁽¹¹⁾

$$E_{EH} = \sum_{k=1} (n_{occ})_k \epsilon_k \quad (5)$$

where $(n_{occ})_k$ is the occupation-number of the k'th molecular orbital, with the E_R interaction energy, Eq. (1) as follows

$$E = E_R + E_{EH} \quad (6)$$

The physical picture that guides the formulation of the ASED method envisions chemical binding as the synthesis of two distinct processes.^(5,13) The molecule is envisioned as being built-up, first,

by the process of bringing together "rigid" and "non-exchanging" atoms. The electrons of each atom are not allowed, at first, to be perturbed by the proximity of other atoms, and neither are the electrons allowed to exchange between the atoms. Once the atoms are thus positioned, the second stage of the molecule-building process is envisioned as allowing the electrons to "delocalize" from the parent atom to all other atoms. In order to isolate the contributions to the energy of the exchange process, effects on the electrons due to fields from neighboring atoms, according to Anderson,⁽¹³⁾ are to be neglected during this second stage. The first process in the build-up of the molecule is envisioned as being energetically unfavorable for binding; the second process is envisioned as being energetically favorable. The balance of these two is envisioned as leading to the equilibrium configuration of the atoms in a molecule.⁽¹³⁾

It is convenient to separate the issue of the validity of the energy ansatz used in the ASED method from that of the usefulness of the physical picture motivating this approach. The ASED method proceeds from the view that chemical bonding is a process ensuing in physically distinct successive stages. This is a theme that has some prospects of having theoretical validity. To illustrate this point, consider reviewing the simple case of bonding in the H_2^+ molecule-ion in the light of the ASED conceptual picture. Let the basis set for the variational energy calculation be a minimal basis set (MBS) consisting of a hydrogen atom orbital centered on each of the nuclei,⁽¹⁴⁾

$$|A\rangle = \frac{1}{\sqrt{\pi}} \exp(-\|r - R_A\|) \quad (7a)$$

$$|B\rangle = \frac{1}{\sqrt{\pi}} \exp(-\|r - R_B\|) \quad (7b)$$

The secular equation is

$$\begin{vmatrix} H_{A,A} - E & H_{A,B} - E S_{A,B} \\ H_{A,B} - E S_{A,B} & H_{A,A} - E \end{vmatrix} = 0 \quad (8)$$

and the lowest-energy solution is⁽¹⁵⁾

$$E = \frac{1}{(1 + S_{A,B})} (H_{A,A} + H_{A,B}) \quad (9)$$

Starting from the usual electronic hamiltonian for this case⁽¹⁵⁾, one obtains

$$H_{A,A} = -I + \langle A | \frac{-1}{\| \chi - R_B \|} + \frac{1}{\| R_A - R_B \|} | A \rangle \quad (10)$$

where $I = -1/2$ hartree = -13.606 eV is the first ionization potential of a hydrogen atom. One recognizes the matrix element on the right-hand-side of Eq. (10) as the E_R energy of the ASED approach. Therefore, we write

$$H_{A,A} = -I + E_R \quad (11)$$

In the case of the H_2^+ molecule-ion, E_p physically corresponds to the classical electrostatic energy for bringing a "rigid" and "non-exchanging" hydrogen atom up to a proton. Hence, we identify the $H_{A,A}$ energy with the first process envisioned in the ASED conceptual picture of bonding. Moreover, in simplifying the expression for E_R one obtains

$$E_R = \int_D^\infty \rho(r) \left(\frac{1}{D} - \frac{1}{r} \right) r^2 dr \quad (12)$$

where $D = \|R_A - R_B\|$ and $\rho(r) = 4 \exp(-2r)$. It is clear from this that $E_R \geq 0$, and that, consistent with the ASED physical picture, E_R is the energetically unfavorable factor for binding.

The $H_{A,B}$ matrix element is the amplitude for the binding electron to make an exchange from basis $|A\rangle$ to basis $|B\rangle$, or, equivalently, to "tunnel" from one atom to the other.⁽¹⁶⁾ Hence, we identify qualitatively the $H_{A,B}$ energy with the second process envisioned in the ASED conceptual picture of bonding. Starting from the usual electronic hamiltonian for this case,⁽¹⁵⁾ one obtains

$$H_{A,B} = -I S_{A,B} + \langle A | \frac{-1}{\|R - R_B\|} + \frac{1}{\|R_A - R_B\|} | B \rangle \quad (13)$$

The evaluation of the matrix element on the right hand-side of Eq. (13) shows that $H_{A,B} \leq 0$ for all except very small internuclear distances.⁽¹⁵⁾ This is consistent with the presumption of the ASED conceptual picture that the energy of the second process would be the energetically favorable one for chemical binding. The identification of the role of exchange matrix elements as the source of chemical binding, of course, has a long and illustrious history.⁽¹⁶⁻²⁰⁾ Finally, these two energetically opposite factors, E_R and $H_{A,B}$, combine directly in Eq. (9) to yield, as envisioned in the ASED conceptual picture, the approximate molecular total energy. There is in Eq. (9) a renormalization factor that does not affect these conclusions since it is a common factor of both E_R and $H_{A,B}$. The dependence on internuclear distance of the competing energies E_R and $H_{A,B}$, and the resultant energy, E , is illustrated in Fig. 1. The symbol Δ in the notation ΔE used in Fig. 1 indicates that the limiting value of E at large internuclear separations has been subtracted. We shall adopt this convention in the rest of this paper.

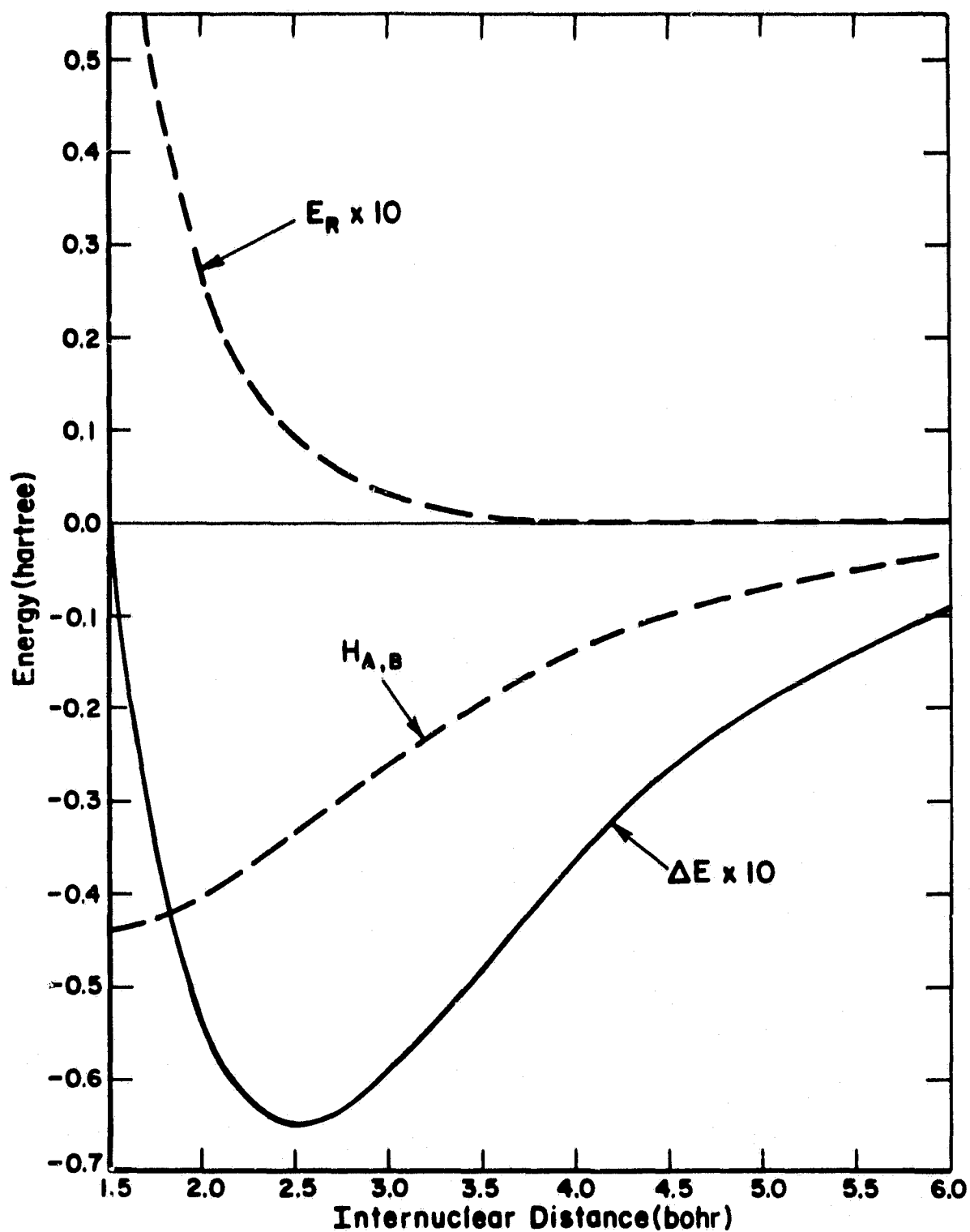


FIG. 1. The electrostatic energy E_R , the exchange energy $H_{A,B}$, and the total energy change ΔE as a function of internuclear distance for the H_2^+ molecule in the $X^2\Sigma_g^+$ state.

The prospects of reconciling Anderson's ASED energy ansatz with that of the MBS variational energy approximation are not good. The ASED energy for this case is

$$E = E_R + \epsilon \quad (14)$$

where

$$\epsilon = \frac{1}{(1 + S_{A,B})} (\bar{H}_{A,A} + \bar{H}_{A,B}) \quad (15)$$

$$\bar{H}_{A,A} = -I \quad (16)$$

$$\bar{H}_{A,B} = -K I S_{A,B} \quad (17)$$

These equations resemble those of Eq. (9) only in form. The irreducible difference lies in the use of the K factor in the ASED exchange matrix element, Eq. (17). This factor controls the contribution of the energy favorable for bonding to the total energy. Moreover, the total energy appears to be very sensitive to small variations in this factor. Figure 2 shows the sensitivity of the ASED potential energy curve for H_2^+ on the choice of the K factor. This figure also illustrates the large differences that can result between the MBS energy curve and the ASED energy curve. This is a numerical indication that the justification for Anderson's ASED energy formulae lies beyond the MBS energy formula. The exact solution may indeed be cast into the form of just a two-state problem by use of the partitioning technique.^(21,22) Such equations are the ultimate basis upon which the validity of the semi-empirical ASED energy formulae can be decided. The analysis of how semi-empirical approximations relate to the exact theoretical basis has been presented before by Freed.⁽²³⁾

To conclude, Fig. 2 also shows, for purposes of comparison, the potential energy curve resulting from an exact numerical solution of the H_2 molecule problem in the $\chi^2_{\Sigma^+}$ state. (24)

III. A FIRST-PRINCIPLES ASSED METHOD

We present below a different molecular-energy decomposition scheme than the traditional one. (1,2) One finds in this decomposition some common elements, however, to the work of Kitaura and Morokuma. (25) In the present work, we have attempted to adhere, as much as we find possible, to the ASSED physical picture of the binding process to motivate the grouping of the various molecular energy terms.

The first task is to find the interaction energy associated with the process of building up the molecule by bringing together "rigid" and "non-exchanging" atoms from infinity to their assigned positions within the molecule. The interaction energy of this process is identified in the ASSED energy *ansatz* with Eq. (1), the E_R energy. Although this was found to be correct in the case of the H_2^+ molecule reviewed above, it does not appear that Eq. (1) is, in general, the correct energy of this process. For instance, a first inspection of Eq. (1) shows that it contains, for each pair of atoms, an arbitrary choice as to which of the two atoms is to be chosen as the source of the electrostatic potential in this formula. It seems unphysical that, in the absence of other factors, the correct interaction should contain an arbitrary choice of this type.

It is possible to show that indeed E_R does not, in general, follow from the premises (5,13) from which it is proposed to be derived. (5,26) Anderson starts the derivation of Eq. (1) by invoking the Hellmann-Feynman force-formula, (27,28)

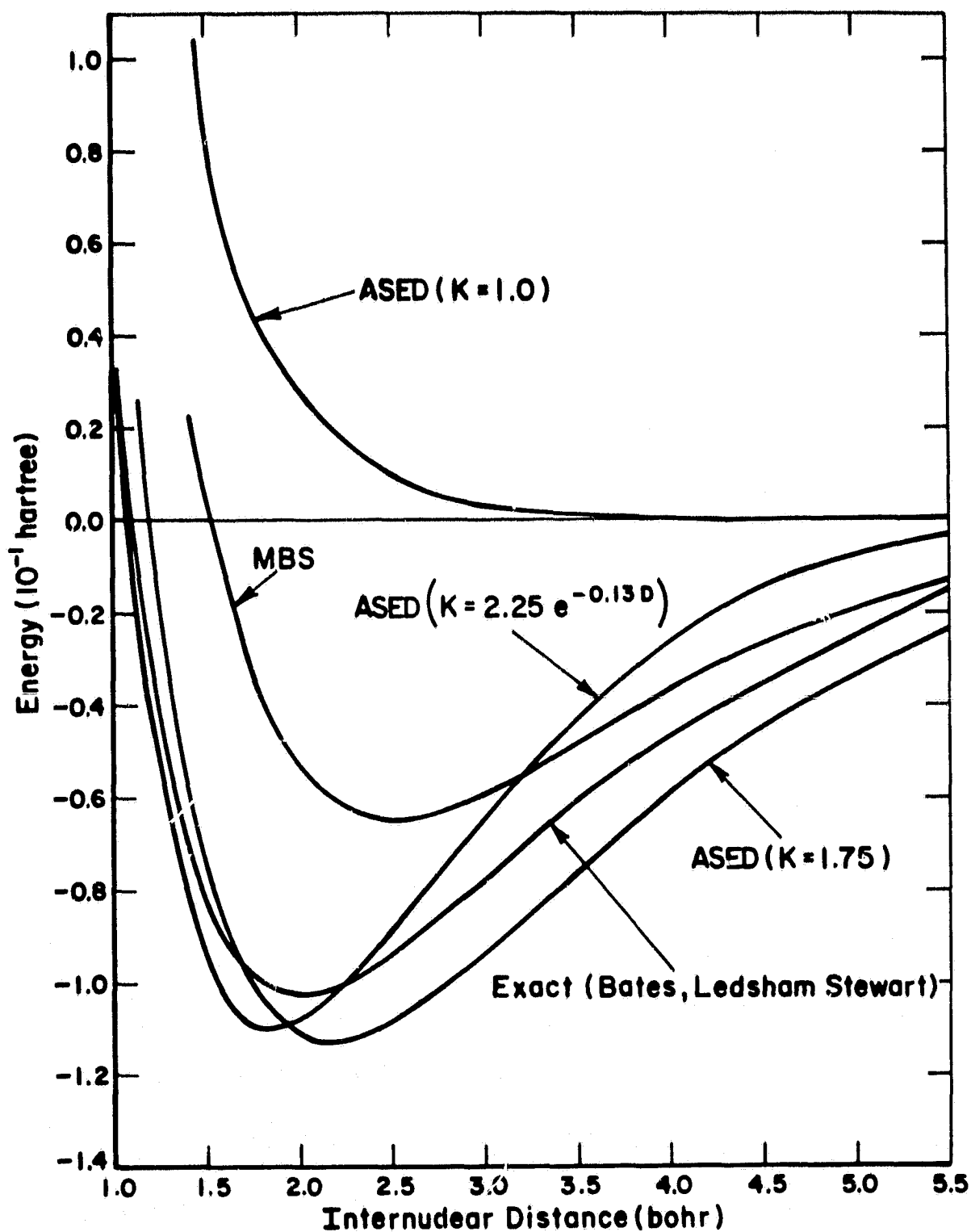


FIG. 2. Comparison of various ASED potential energy curves for the H_2^+ molecule in the $X^2\Sigma_g^+$ state with the minimum basis set variational energy⁽¹⁵⁾ and the exact potential energy curve.⁽²⁴⁾

$$\nabla_A E = Z_A \left(\sum_{B \neq A} Z_B \frac{(\mathbf{R}_B - \mathbf{R}_A)}{\|\mathbf{R}_B - \mathbf{R}_A\|^3} - \int \rho(\mathbf{r}) \frac{(\mathbf{r} - \mathbf{R}_A)}{\|\mathbf{r} - \mathbf{R}_A\|^3} d\mathbf{r} \right) \quad (18)$$

where ∇_A is the gradient operator with respect to the three components of the position vector \mathbf{R}_A , and $\rho(\mathbf{r})$ is the exact molecular one-electron density. The exact density is then written in terms of the superposition of atomic densities and a complementary term,

$$\rho(\mathbf{r}) = \sum_B \rho_B^{\text{at}}(\mathbf{r} - \mathbf{R}_B) + \delta\rho(\mathbf{r}) \quad (19)$$

In order to isolate the energy resulting solely from the superposition of the "rigid" atoms, Anderson advocates^(5,13,26) neglecting in Eq. (18) all terms not arising from the superposition of atomic densities in $\rho(\mathbf{r})$. The result, which we denote $\nabla_A E_R$, is

$$\nabla_A E_R = Z_A \left(\sum_{B \neq A} Z_B \frac{(\mathbf{R}_B - \mathbf{R}_A)}{\|\mathbf{R}_B - \mathbf{R}_A\|^3} - \sum_B \int \rho_B^{\text{at}}(\mathbf{r} - \mathbf{R}_B) \frac{(\mathbf{r} - \mathbf{R}_A)}{\|\mathbf{r} - \mathbf{R}_A\|^3} d\mathbf{r} \right) \quad (20)$$

Note that, because each atomic density is of even parity under inversion through its own center,

$$\int \rho_A^{\text{at}}(\mathbf{r} - \mathbf{R}_A) \frac{(\mathbf{r} - \mathbf{R}_A)}{\|\mathbf{r} - \mathbf{R}_A\|^3} d\mathbf{r} = 0 \quad (21)$$

Using this result, one may write Eq. (20) in a more compact form

$$\nabla_A E_R = Z_A \sum_{B \neq A} \int \rho_B(\mathbf{r} - \mathbf{R}_B) \frac{(\mathbf{r} - \mathbf{R}_A)}{\|\mathbf{r} - \mathbf{R}_A\|^3} d\mathbf{r} \quad (22)$$

where

$$\rho_B(\chi - R_B) = Z_B \delta(\chi - R_B) - \rho_B^{\text{at}}(\chi - R_B) \quad (23)$$

The function E_R is obtained from the gradients of Eq. (22) by a line integral along a path taking the system from infinity to its assigned configuration in the molecule,

$$E_R = \int_{\infty}^{\chi} \sum_A \nabla_A E_R \cdot dR_A \quad (24)$$

This reduces, after some manipulation, to

$$E_R = \sum_{A > B} \left[Z_B \left(\frac{Z_A}{\|R_A - R_B\|} - \int \frac{\rho_A^{\text{at}}(\chi - R_A)}{\|\chi - R_A\|} d\chi \right) + \int \left[Z_A \rho_B^{\text{at}}(\chi) - Z_B \rho_A^{\text{at}}(\chi) \right] \left(\int_{\infty}^1 d\lambda \frac{(\chi + (R_B - R_A)\lambda) \cdot R_A}{\|\chi + (R_B - R_A)\lambda\|^3} \right) d\chi \right] \quad (25)$$

The remaining integral over the λ variable is a standard integral. (29)

The result is a complicated combination of terms the details of which become unimportant here. The point to note is that the summand in Eq. (25) is symmetric upon permutation of atom labels A and B. Thus, the problem with the arbitrary choice in the heretofore used formula for E_R , Eq. (1), is resolved. The corrected equation also shows that, if the atoms of a particular pair are identical, then the formula for that pair interaction reduces to just that obtained from Eq. (1).

However, even the corrected expression for E_R , Eq. (25), does not fully correspond to the energy of the physical process of building up the molecule from "rigid" and "non-exchanging" atoms. The source

of the problem is that, when an approximate one-electron density, such as the superposition of atomic densities, is used, then, the Hellmann-Feynman formula, Eq. (18), only yields a part of the gradient of the energy.⁽³⁰⁾ The other part of the gradient of the energy derives from the terms involving the partial derivatives of the wavefunction. There is in this case, no apparent physical justification for neglecting this other part. The total gradient, which we denote $\nabla_A E_{cl}$, in this case is

$$\begin{aligned} \nabla_A E_{cl} = & \nabla_A E_R + \sum_{B \neq A} \left(\int \frac{-Z_B}{\|\chi - R_B\|} \nabla_A \rho_A^{at}(\chi - R_A) d\chi \right. \\ & \left. + \iint \frac{1}{\|\chi - \chi'\|} \rho_B^{at}(\chi - R_B) \nabla_A \rho_A^{at}(\chi' - R_A) d\chi d\chi' \right) \end{aligned} \quad (26)$$

where $\nabla_A E_R$ is given by Eq. (22). After some algebraic manipulation, one obtains

$$\nabla_A E_{cl} = \sum_{B \neq A} \iint \frac{(\chi - \chi')}{\|\chi - \chi'\|^3} \rho_A(\chi' - R_A) \rho_B(\chi - R_B) d\chi d\chi' \quad (27)$$

where the density $\rho_A(\chi' - R_A)$, for example, is defined by Eq. (23).

Proceeding just as before, one obtains the energy E_{cl} from the gradient, $\nabla_A E_{cl}$, by a line integration, e.g. Eq. (24). The result is

$$E_{cl} = \frac{1}{2} \sum_A \sum_{B \neq A} \iint \frac{\rho_A(\chi - R_A) \rho_B(\chi' - R_B)}{\|\chi - \chi'\|} d\chi d\chi' \quad (28)$$

This is just the energy expression expected from classical electrostatics. It is the work of assembling "frozen" charge distributions $\rho_A(\chi - R_A)$ by the process of bringing each one successively from infinity

to its assigned position in the presence of the electric field of the "frozen" charge distributions already assembled.⁽³¹⁾ It therefore seems that E_{el} , rather than E_R , best satisfies the requirements of the correct energy expression for the first stage of bonding of the ASED approach.

The next step is to incorporate the E_{el} energy into the molecular energy. The expression for the molecular total energy is^(15,22)

$$E = E_{el} + \sum_{A > B} \sum \frac{Z_A Z_B}{\|R_A - R_B\|} \quad (29)$$

The exact electronic energy may be written as the expectation value

$$E_{el} = \langle \Psi | \hat{H} | \Psi \rangle / \langle \Psi | \Psi \rangle \quad (30)$$

where, as usual, the exact many-electron molecular hamiltonian, \hat{H} , is the sum, over all electrons, of the kinetic-energy, nuclear-attraction, and electron-repulsion operators^(15,22)

$$\hat{H} = \sum_i \hat{h}(i) + \sum_{i > j} \sum \frac{1}{\|r_i - r_j\|} \quad (31a)$$

$$\hat{h} = -\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{\|r - R_A\|} \quad (31b)$$

The exact many-electron wavefunction, Ψ , is one of the eigenfunctions of the hamiltonian operator, \hat{H} . The particular electronic state to which E_{el} refers to is dictated by the choice of the eigenfunction Ψ . Consider constructing the following combination of terms, which we label D,

$$\begin{aligned}
 D = & \frac{1}{2} \sum_A \sum_B \left(-z_B \int \frac{\rho_A^{\text{at}}(\chi - R_A)}{\|\chi - R_B\|} d\chi - z_A \int \frac{\rho_B^{\text{at}}(\chi - R_B)}{\|\chi - R_A\|} d\chi \right. \\
 & \left. + \iint \frac{\rho_A^{\text{at}}(\chi - R_A) \rho_B^{\text{at}}(\chi' - R_B)}{\|\chi - \chi'\|} d\chi d\chi' \right) \quad (32)
 \end{aligned}$$

Adding and subtracting the term D from the right-side of Eq. (29) yields the molecular total energy in the form

$$E = E_{\text{cl}} + E_{\text{el}} - D \quad (33)$$

where E_{cl} is defined by Eq. (28). As discussed above, E_{el} is the term that physically is identified with the first-stage of bonding in the ASFD approach.

In order to show how the D term combines with the E_{el} term, we construct a convenient energy decomposition scheme. We partition the many-electron hamiltonian into a zero-order hamiltonian, $\hat{H}^{(0)}$, and a perturbation, $\hat{H}^{(1)}$,

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} \quad (34)$$

where the terms of the partitioned hamiltonian are defined as

$$\hat{H}^{(0)} = \sum_i \left(\hat{h}(i) + \hat{v}(i) \right) \quad (35)$$

and

$$\hat{H}^{(1)} = \sum_{i > j} \sum \frac{1}{\|\mathbf{r}_i - \mathbf{r}_j\|} - \sum_i \hat{v}(i) \quad (36)$$

This type of partition is well-known from perturbation-theory approaches to the electron-correlation problem.⁽³²⁻³⁴⁾ In the electron-correlation problems, \hat{v} is usually chosen as some form of the Hartree-Fock potential. For a closed-shell system, for example, this is^(22,32)

$$\hat{v} = \sum_k \left(2 \hat{J}_k - \hat{K}_k \right) \quad (37a)$$

where the Coulomb and exchange operators are defined respectively as

$$\hat{J}_k = \int dx_1 \frac{1}{\|x_1 - x_2\|} \psi_k(x_1) \psi_k(x_2) \quad (37b)$$

$$\hat{K}_k = \int dx_1 \frac{1}{\|x_1 - x_2\|} \psi_k(x_1) \hat{\tau}_{12} \psi_k(x_2) \quad (37c)$$

The summation ranges over all occupied Hartree-Fock molecular orbitals, $\psi_k(x)$. In the present case, consistent with the physical picture of the first-stage of bonding of the ASED approach, we define \hat{v} instead as a superposition of atomic potentials, each centered on its own atomic nucleus,

$$\hat{v} = \sum_A \hat{v}_A^{\text{at}} \quad (38)$$

There is no unique choice of the atomic one-electron potentials \hat{v}_A^{at} . Physically, we wish these potentials to enable an electron of the molecule, when in the vicinity of one of the atoms, to interact with the electrons of this atom as though it were part of the electronic structure of this atom.⁽³⁵⁾ In the Hartree-Fock approximation, the potential meeting this physical criterion (in a closed-shell system) is given by Eq. (37) but as constructed from atomic-orbitals rather than molecular-orbitals. In more accurate approximations, a similar

atomic potential exists but its form may be much more complex. In general, an approximation for an n_A -electron atomic system which retains an independent-particle interpretation will have at most n_A different atomic orbitals. Each of these different atomic orbitals can be interpreted as the state of an electron moving in the field due to the other electrons. That is, each atomic orbital, $\phi_{k,A}$, is the solution of an equation

$$\left(-\frac{1}{2} \nabla^2 - \frac{Z_A}{\|x - R_A\|} + \hat{U}_{k,A} \right) \phi_{k,A} = \epsilon_{k,A} \phi_{k,A} \quad (39)$$

where $\hat{U}_{k,A}$ contains the interaction effects due to the other (n_A-1) electrons of the atom. Each occupied orbital is associated with its own characteristic (n_A-1) -electron potential $\hat{U}_{k,A}$. To accommodate the specificity of each potential to its atomic orbital, we write, in general,

$$\hat{v}_A^{\text{at}} = \sum_k \hat{U}_{k,A} |\phi_{k,A}\rangle \langle \phi_{k,A}| \quad (40)$$

where we implicitly assume in writing the equations in this form that the atomic orbitals, $\phi_{k,A}$, form an orthonormal set of functions. In the case that these orbitals are non-orthogonal, a somewhat more complicated expression applies. Note that the summation in Eq. (40) is, in principle, not restricted to just the n_A occupied atomic orbitals. In practice, however, one may obtain a manifold of physically meaningful unoccupied levels from the potentials for the energetically-highest occupied orbitals.⁽³⁶⁾ For example, one may in such a case write Eq. (40) as

$$\hat{v}^{\text{at}} = \hat{U}_{n,A} + \sum_{k=1}^n \left(\hat{U}_{k,A} - \hat{U}_{n,A} \right) |\phi_{k,A}\rangle \langle \phi_{k,A}| \quad (41)$$

The partition of the electronic hamiltonian into a zero-order hamiltonian, $\hat{H}^{(0)}$, and a perturbation, $\hat{H}^{(1)}$, are the basic ingredients defining a perturbation expansion of the electronic energy, Eq. (30), as follows

$$E_{el} = E_{el}^{(0)} + E_{el}^{(1)} + E_{el}^{(2)} + E_{el}^{(3)} + \dots \quad (42)$$

The zero-order energy, $E_{el}^{(0)}$, is the eigenvalue of the zero-order hamiltonian $\hat{H}^{(0)}$. An eigenfunction of $\hat{H}^{(0)}$ is a product of N one-electron functions

$$\phi(x_1, x_2, \dots, x_N) = \psi_1(x_1) \psi_2(x_2) \dots \psi_N(x_N) \quad (43)$$

where the one-electron functions, $\psi_k(x)$, are eigenfunctions of the equation

$$\left[-\frac{1}{2} \nabla^2 + \sum_A \left(-\frac{Z_A}{\|x - R_A\|} + \hat{v}_A^{\text{at}} \right) \right] \psi_k(x) = \epsilon_k \psi_k(x) \quad (44)$$

N is the number of electrons in the molecule. The actual distinct number of occupied orbitals appearing in the basic product wavefunction, Eq. (43), is determined by the usual building-up principle of occupying the energy levels, ϵ_k , in order of increasing energy and in accordance with the Pauli-principle. The zero-order energy is thus the sum of the one-electron molecular orbital energies

$$E_{el}^{(0)} = \sum_k (n_{\text{occ}})_k \epsilon_k \quad (45)$$

where $(n_{\text{occ}})_k$ is the occupation number of the k'th molecular orbital level, and the summation ranges only over the occupied levels. Although ϕ is an eigenfunction of $\hat{H}^{(0)}$, any permutation of the

electron-coordinates also produces a degenerate eigenfunction. The physically most complete eigenfunction of $\hat{H}^{(0)}$ is therefore, an anti-symmetric combination of these products which is an eigenfunction of spin, ⁽³⁷⁾ i.e.

$$\psi^{(0)} = A \left[\phi \left(\sum_i c_i \theta_i^{S,N} \right) \right] \quad (46)$$

where A is the antisymmetrizer, and $\theta_i^{S,N}$ is a linear combination of N-electron spin-function products which yield spin

$$\hat{S}^2 \theta_i^{S,N} = S(S+1) \theta_i^{S,N} \quad (47)$$

we indicate a sum over spin-eigenfunctions $\theta_i^{S,N}$ in Eq. (46) since, as is well known, there are generally several linearly independent spin eigenfunctions of spin S arising from the coupling of N spin-1/2 particles. ⁽³⁷⁾

Expanding the molecular-orbitals, ψ_k , in terms of a basis set of atom-centered functions, $\chi_{\mu,A}$,

$$\psi_k = \sum_A \sum_{\mu \in S_A} \chi_{\mu,A} (r - R_A) c_{\mu,A;k} \quad (48)$$

leads from Eq. (44) to a matrix-equation such as Eq. (2). The hamiltonian matrix-elements are defined as

$$H_{\mu,A;\nu,B} = \langle \chi_{\mu,A} | -\frac{1}{2} \nabla^2 + \sum_C \left(-\frac{Z_C}{\|r - R_C\|} + \hat{v}_C^{\text{at}} \right) | \chi_{\nu,B} \rangle \quad (49)$$

The evaluation of the matrix elements of the usual one-electron operators poses no particular problem. The matrix elements of the atomic one-electron potential, \hat{v}_C^{at} , may be evaluated conveniently by

preparing, from the atomic orbital basis, a matrix-representation of the short-range part of the potential. For example, define an effective charge as

$$\zeta_A(\mathbf{r} - \mathbf{R}_A) \equiv (n_A - 1) \left[1 - \exp(-\alpha \|\mathbf{r} - \mathbf{R}_A\|^2) \right] \quad (50)$$

where n_A is the number of electrons on the A'th atom. The parameter α is defined so that the onset of the asymptotic behavior of ζ_A ,

$$\zeta_A(r) \sim (n_A - 1) \quad (51a)$$

coincides with the onset of the asymptotic behavior of $\hat{U}_{k,A}$,

$$\hat{U}_{k,A} \sim \frac{(n_A - 1)}{r} \quad (51b)$$

The difference potential,

$$\hat{U}_{k,A} - \frac{\zeta_A(\mathbf{r} - \mathbf{R}_A)}{\|\mathbf{r} - \mathbf{R}_A\|} \quad , \quad (52)$$

is then defined as the short-range part of the $\hat{U}_{k,A}$ potential. This short-range potential may be represented in a basis centered only on the origin of the potential. We write this representation as

$$\hat{U}_{k,A} - \frac{\zeta_A(\mathbf{r} - \mathbf{R}_A)}{\|\mathbf{r} - \mathbf{R}_A\|} = \sum_{\ell \in S_A} \sum_{\ell' \in S_A} |\phi_{\ell,A}\rangle M_{\ell,\ell'}^{(k)} \langle \phi_{\ell',A}| \quad (53)$$

where

$$M_{\ell,\ell'}^{(k)} = \int \phi_{\ell,A}(\mathbf{r}) \left(\hat{U}_{k,A} - \frac{\zeta_A(r)}{r} \right) \phi_{\ell',A}(\mathbf{r}) \, d\mathbf{r} \quad (54)$$

The convergence of this representation is expected to be rapid given the generally slowly varying character that is typical of $\hat{U}_{k,A}$ potentials in this inner range. Therefore, we expect that restriction of the

representation to a finite basis yields a reliable approximation of the short-range properties of the potential. The net expression for the hamiltonian matrix elements is

$$H_{\mu,A;\nu,B} = \langle \chi_{\mu,A} | -\frac{1}{2} \nabla^2 + \sum_C \left(-\frac{(Z_C - \zeta_C)}{\|\mathbf{r} - \mathbf{R}_C\|} \right. \\ \left. + \sum_{\ell \in S_C} \sum_{\ell' \in S_C} |\phi_{\ell,C}\rangle M_{\ell,\ell'}^{(\ell')} \langle \phi_{\ell',C}| \right) | \chi_{\nu,B} \rangle \quad (55)$$

If the basis functions $\chi_{\mu,A}$ are chosen as the atomic orbitals, then the expression for the hamiltonian matrix elements takes on yet another simple form. We find

$$H_{\mu,A;\nu,A} = \epsilon_{\nu,A} \delta_{\mu,\nu} + \langle \phi_{\mu,A} | \sum_{C \neq A} \left(-\frac{Z_C}{\|\mathbf{r} - \mathbf{R}_C\|} + \hat{v}_C^{\text{at}} \right) | \phi_{\nu,A} \rangle \quad (56)$$

and

$$H_{\mu,A;\nu,B} = \frac{1}{2} (\epsilon_{\mu,A} + \epsilon_{\nu,B}) S_{\mu,A;\nu,B} + \frac{1}{2} \langle \phi_{\mu,A} | \left(-\frac{Z_A}{\|\mathbf{r} - \mathbf{R}_A\|} + \hat{v}_A^{\text{at}} \right) \\ + \left(-\frac{Z_B}{\|\mathbf{r} - \mathbf{R}_B\|} + \hat{v}_B^{\text{at}} \right) | \phi_{\nu,B} \rangle + \langle \phi_{\mu,A} | \sum_{\substack{C \neq A \\ C \neq B}} \left(-\frac{Z_C}{\|\mathbf{r} - \mathbf{R}_C\|} + \hat{v}_C^{\text{at}} \right) | \phi_{\nu,B} \rangle \quad (57)$$

The one-electron energies, $\epsilon_{\mu,A}$, are approximations to the true ionization potentials of the atoms.⁽³⁸⁾ Hence, through Eqs. (56) and (57), the hamiltonian matrix has a superficial resemblance to the corresponding matrix in the ASED approach as defined by Eqs. (3a) and (3b). If the one-electron atomic potential, Eq. (40), can be reduced to one common potential for all atomic orbitals, then one obtains, even for an arbitrary basis, the simple result

$$\begin{aligned}
H_{\mu,A;\nu,B} = & \sum_k \epsilon_{k,A} \langle \chi_{\mu,A} | \phi_{k,A} \rangle \langle \phi_{k,A} | \chi_{\nu,B} \rangle \\
& + \langle \chi_{\mu,A} | \sum_{C \neq A} \left(-\frac{z_C}{\|\mathbf{r} - \mathbf{R}_C\|} + \hat{U}_C \right) | \chi_{\nu,B} \rangle
\end{aligned} \tag{58}$$

Any of these formulae are very convenient, from a practical point of view, because their calculation, we note, requires at most the evaluation of one-electron-type integrals.

Thus far we have established the basis for a convenient decomposition of the exact molecular total energy into the form

$$E = E_{el} + E_{el}^{(0)} + E_{el}^{(1)} - D + E_{el}^{(2)} + E_{el}^{(3)} + \dots \tag{59}$$

We find that the first two terms, $E_{el} + E_{el}^{(0)}$, have a resemblance to the semi-empirical ASED energy formulae, Eq. (6). We consider next the terms in Eq. (59) that are required to improve the approximation. In particular, we consider the nature of the first-order energy and its combination with the D term. The first-order energy is defined as

$$E_{el}^{(1)} = \langle \psi^{(0)} | \hat{H}^{(1)} | \psi^{(0)} \rangle / \langle \psi^{(0)} | \psi^{(0)} \rangle \tag{60}$$

This energy may be written generally as⁽²²⁾

$$E_{el}^{(1)} = \frac{1}{2} \iint \frac{1}{\|\mathbf{r} - \mathbf{r}'\|} \rho^{(2)}(\mathbf{r}, \mathbf{r}'; \mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' - \sum_A \int_{\mathbf{r}' = \mathbf{r}} \hat{v}_A^{\text{at}} \rho^{(1)}(\mathbf{r}, \mathbf{r}') d\mathbf{r} \tag{61}$$

where $\rho^{(2)}(\mathbf{r}, \mathbf{r}'; \mathbf{r}, \mathbf{r}')$ is the diagonal component of the two-electron density matrix after integration over the spin variables⁽²²⁾, and $\rho^{(1)}(\mathbf{r}, \mathbf{r}')$ is the one-electron density matrix, also after integration

over the spin variables.⁽²²⁾ Note that we shall adopt the convention to denote the diagonal component of the one-electron density-matrix, namely $\rho^{(1)}(r, r)$, as simply $\rho(r)$. This is also, in fact, just the electron-density function we have been using in the foregoing discussions. To proceed, we find it convenient to designate a part of the two-electron integral in Eq. (61) as a Coulomb energy, and the remainder, as an exchange energy. For this purpose, we use the device of defining formally a two-electron correlation function as⁽³⁹⁾

$$c^{(2)}(r, r'; r, r') \equiv \rho^{(2)}(r, r'; r, r') - \rho(r)\rho(r') \quad (62)$$

In terms of this definition, the first-order energy assumes the conceptually convenient form

$$E_{el}^{(1)} = \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{\|r - r'\|} dr dr' - \sum_{r'=r} \int \hat{v}_A^{at} \rho^{(1)}(r, r') dr + E_{xch} \quad (63)$$

where

$$E_{xch} = \frac{1}{2} \iint \frac{c^{(2)}(r, r'; r, r')}{\|r - r'\|} dr dr' \quad (64)$$

The D term, Eq. (32), may also be written in the convenient form

$$D = \sum_A \left(-Z_A \int dr \left[\rho^{sup}(r) - \rho_A^{at}(r-R_A) \right] / \|r - R_A\| \right) \\ + \frac{1}{2} \iint dr dr' \left[\rho^{sup}(r)\rho^{sup}(r') - \sum_A \rho_A^{at}(r-R_A)\rho_A^{at}(r'-R_A) \right] / \|r - r'\| \quad (65)$$

where $\rho^{\text{sup}}(r)$ is defined as the superposition of atomic densities,

$$\rho^{\text{sup}}(r) = \sum_A \rho_A^{\text{at}}(r - R_A) \quad (66)$$

Combining Eqs. (63) and (65) to obtain the expression for $(E_{el}^{(1)} - D)$, we find

$$\begin{aligned} E_{el}^{(1)-D} = & -\sum_A \int_{r'=r} \left(-\frac{Z_A}{\|r - R_A\|} + \hat{v}_A^{\text{at}} \right) \rho^{(1)}(r, r') dr + E_{xc}^{(1)} \\ & -\sum_A \int \frac{Z_A}{\|r - R_A\|} [\rho(r) - \rho^{\text{sup}}(r)] dr \\ & + \frac{1}{2} \iint \frac{1}{\|r - r'\|} [\rho(r)\rho(r') - \rho^{\text{sup}}(r)\rho^{\text{sup}}(r')] dr dr' \\ & -\sum_A \int \frac{Z_A}{\|r - R_A\|} \rho_A^{\text{at}}(r - R_A) dr \\ & + \frac{1}{2} \sum_A \iint \frac{1}{\|r - r'\|} \rho_A^{\text{at}}(r - R_A) \rho_A^{\text{at}}(r' - R_A) dr dr' \quad (67) \end{aligned}$$

Having completed the definition of $(E_{el}^{(1)} - D)$, we seek to combine the energy terms of the zero-order energy, $E_{el}^{(0)}$, with the terms in $(E_{el}^{(1)} - D)$. First we note that $E_{el}^{(0)}$, Eq. (45), may also be written as

$$E_{el}^{(0)} = \int_{r'=r} \left[-\frac{1}{2} \nabla^2 + \sum_A \left(-\frac{Z_A}{\|r - R_A\|} + \hat{v}_A^{\text{at}} \right) \right] \rho^{(1)}(r, r') dr \quad (68)$$

Combining this formula for $E_{el}^{(0)}$ with $(E_{el}^{(1)} - D)$, Eq. (67), results in the cancellation of some terms. The net resulting formula is

$$E_{el}^{(0)} + E_{el}^{(1)} - D = \delta E_{el}^{(0+1)} + \delta^2 E_{el}^{(0+1)} + E_{el}^{at} + E_{xcl}^{(1)} \quad (69)$$

where

$$\delta E_{el}^{(0+1)} = \int_{x'=x} \left(\hat{h} + \int \frac{1}{\|x-x''\|} \rho^{sup}(x'') dx'' \right) \delta \rho^{(1)}(x, x') dx \quad (70)$$

and

$$\delta^2 E_{el}^{(0+1)} = \frac{1}{2} \iint \frac{1}{\|x-x'\|} \delta \rho^{(1)}(x) \delta \rho^{(1)}(x') dx dx' \quad (71)$$

and

$$E_{el}^{at} = \sum_A \left[\int_{x'=x} \left(-\frac{1}{2} \nabla^2 - \frac{Z_A}{r} \right) \rho_A^{at}(x, x') dx \right. \\ \left. + \frac{1}{2} \iint \frac{1}{\|x-x'\|} \rho_A^{at}(x) \rho_A^{at}(x') dx dx' \right] \quad (72)$$

Equations (70) and (71) give the effect on the energy of the change in the one-electron density matrix relative to the superposition of atomic densities. The relaxation in the density matrix is defined as

$$\delta \rho^{(1)}(x, x') = \rho^{(1)}(x, x') - \rho^{sup}(x, x') \quad (73)$$

Note that

$$\int \delta \rho^{(1)}(x) dx = 0 \quad (74)$$

The term $E_{el}^{(0+1)}$ represents the linear effect on the kinetic, electron-nuclear attraction, and Coulomb electron-electron interaction energies

due to relaxation of the electron density. The term $\delta_{el}^2 E^{(0+1)}$ is the non-linear relaxation effect. Both $\delta E_{el}^{(0+1)}$ and $\delta^2 E_{el}^{(0+1)}$, the same as E_{el} , approach zero as the atoms separate to the neutral-atoms limit. The E_{el}^{at} energy is constant with changes in molecular geometry. It is the sum of the kinetic, electron-nuclear attraction, and Coulomb electron-electron repulsion energies of the isolated atoms.

The formulation of the sum $(E_{el}^{(0)} + E_{el}^{(1)})$ remains incomplete without a more precise definition of the exchange energy, $E_{xch}^{(1)}$. For this purpose it is necessary to specify in greater detail the structure of the zero-order wavefunction $\psi^{(0)}$, Eq. (46). Let the orbital product ϕ in the zero-order wavefunction be composed of n doubly occupied orbitals and m singly occupied orbitals,

$$\phi = \psi_1^2 \psi_2^2 \cdots \psi_n^2 \psi_{n+1} \psi_{n+2} \cdots \psi_{n+m} \quad (75)$$

where $2n+m = N$. The one-electron density matrix resulting from this wavefunction, Eqs. (46) and (75), is

$$\rho^{(1)}(r, r') = 2 \sum_{k=1}^n \psi_k(r) \psi_k(r') + \sum_{k=1}^m \psi_{k+n}(r) \psi_{k+n}(r') \quad (76)$$

The exchange energy associated with this wavefunction is⁽⁴⁰⁾

$$E_{xch}^{(1)} = - \sum_{k=1}^n \sum_{\ell=1}^n K_{k,\ell} - \sum_{k=1}^m \sum_{\ell=1}^n K_{k+n,\ell} + \frac{1}{2} \sum_{k=1}^m \sum_{\ell=1}^m g_{k\ell} K_{k+n,\ell+n} \quad (77)$$

where

$$g_{k\ell} = \sum_{i=1}^{n_s} \sum_{j=1}^{n_s} c_i U_{ij}^{S,m}(\tau_{k\ell}) c_j \quad k \neq \ell \quad (78a)$$

$$= 1 \quad k = \ell \quad (78b)$$

The $K_{k,\ell}$ in Eq. (70) are just the exchange integrals defined, as usual, by

$$K_{k,\ell} = \iint \frac{\psi_k(x)\psi_\ell(x)\psi_k(x')\psi_\ell(x')}{\|x-x'\|} dx dx' \quad (79)$$

All the properties pertaining to the total spin of the system, S , and to the relative weight of each alternative linearly independent spin coupling of the m unpaired orbitals are contained in the $g_{k\ell}$ coefficient.⁽⁴⁰⁾ The number of these linearly-independent spin-couplings is denoted by n_s . The value of n_s is determined by the desired total spin and the number, m , of unpaired orbitals. It is given by⁽²²⁾

$$n_s = \frac{(2S+1)m!}{(\frac{1}{2}m+S+1)!(\frac{1}{2}m-S)!} \quad (80)$$

The properties of the $g_{k\ell}$ coefficients have been discussed extensively by Goddard, Ladner, and Bobrowicz.^(37,40) The c_i in the expression for $g_{k\ell}$ give the relative contribution in the total wavefunction of each alternative spin-coupling. They are obtained from the eigenvectors of the secular equation

$$\sum_{j=1}^{n_s} \left[\left(\sum_{k>}^m \sum_{\ell}^m U_{ij}^{S,m} (\hat{\tau}_{k\ell})^{K_{k+n, \ell+n}} \right) - \Lambda_k \delta_{ij} \right] c_{j;k} = 0 \quad i, k=1, \dots, n_s \quad (81a)$$

The eigenvalue Λ_k is the energy difference

$$\Lambda_k = (E_{el}^{(0)} + E_{el}^{(1)}) - E_{el}^* \quad (81b)$$

The energy E_{el}^* is independent of the details due to spin and spin-coupling. It is only dependent on the number of doubly and singly occupied orbitals in orbital product, Eq. (75). It is given by⁽⁴⁰⁾

$$\begin{aligned}
E_{el}^* = & 2 \sum_{k=1}^n \langle \psi_k | \hat{h} | \psi_k \rangle + \sum_{k=1}^m \langle \psi_{k+n} | \hat{h} | \psi_{k+n} \rangle + \sum_{k=1}^n \sum_{\ell=1}^n (2J_{k,\ell} - K_{k,\ell}) \\
& + \sum_{k=1}^m \sum_{\ell=1}^n (2J_{k+n,\ell} - K_{k+n,\ell}) + \frac{1}{2} \sum_{k=1}^m \sum_{\ell=1}^m J_{k+n,\ell+n} \quad (82)
\end{aligned}$$

where the one-electron operator \hat{h} is defined in Eq. (31b), and the Coulomb integrals are defined, as usual, by

$$J_{k,\ell} = \iint \frac{\psi_k^2(x) \psi_\ell^2(x')}{\|x - x'\|} dx dx' \quad (83)$$

The average energy of the n_s possible spin-coupling states follows from Eqs. (81) and (82). It is

$$(E_{el}^{(0)} + E_{el}^{(1)})_{avg} = E_{el}^* + \sum_{k>}^m \sum_{\ell}^m \bar{x}^{S,m}(\hat{\tau}_{k\ell}) K_{k+n,\ell+n} \quad (84a)$$

where

$$\bar{x}^{S,m}(\hat{\tau}_{k\ell}) = \sum_{i=1}^{n_s} U_{ii}^{S,m}(\hat{\tau}_{k\ell}) / n_s \quad (84b)$$

All the information about total spin and spin coupling affecting the total energy resides in the $U_{ij}^{S,m}(\hat{\tau}_{k\ell})$ matrix elements. These are the elements of orthogonal matrices that yield the irreducible representations of the symmetric group, S_m , based on standard Young shapes and tableaux. (37,40,41) The matrix elements used here belong to the matrix representation of the elementary transpositions $\hat{\tau}_{k\ell}$. $\bar{x}^{S,m}(\hat{\tau}_{k\ell})$ of Eq. (84) is, apart from the n_s divisor, just the character of the (S,m) irreducible representation for the $\hat{\tau}_{k\ell}$ element of S_m .

The exchange energy can also, at least formally, be decomposed into a term constructed from the limiting orbitals to which the molecular orbitals tend as the atoms separate, E_{xch}^0 , and terms that give the relaxation effects relative to the first term,

$$E_{xch}^{(1)} = E_{xch}^0 + \delta E_{xch}^{(1)} + \delta^2 E_{xch}^{(1)} \quad (85)$$

Let the set of molecular orbitals $\{\psi_k\}$ become the set of limit orbitals $\{\psi_k^0\}$ as the atoms separate. Then E_{xch}^0 is given by Eq. (77) but replacing the ψ_k orbitals with the limit orbitals ψ_k^0 to construct the various terms. The relaxation energy in turn is

$$\begin{aligned} \delta E_{xch}^{(1)} = & \sum_{k=1}^n \int_{\chi=\chi'}^{\chi=\chi'} \left(- \sum_{\ell=1}^n \hat{K}_{\ell}^0 - \frac{1}{2} \sum_{\ell=1}^m K_{\ell+n}^0 \right) \delta \rho_k^{(1)}(\chi, \chi') d\chi \\ & + \sum_{k=1}^m \int_{\chi=\chi'}^{\chi=\chi'} \left(- \sum_{\ell=1}^n \hat{K}_{\ell}^0 + \sum_{\ell=1}^m g_{k\ell} \hat{K}_{\ell+n}^0 \right) \delta \rho_{k+n}^{(1)}(\chi, \chi') d\chi \quad (86) \end{aligned}$$

where

$$\delta \rho_k^{(1)}(r, r') = (n_{occ})_k (\psi_k(r)\psi_k(r') - \psi_k^0(r)\psi_k^0(r')) \quad (87)$$

and

$$(n_{occ})_k = 2 \quad 1 < k < n \quad (88a)$$

$$= 1 \quad n+1 < k < n+m \quad (88b)$$

The \hat{K}_{ℓ}^0 are just the usual exchange operators, Eq. (37c). The superscript is used here to indicate that the orbitals used to construct \hat{K}_{ℓ}^0 are the limit orbitals $\{\psi_{\ell}^0\}$. The non-linear relaxation effect on the energy is

$$\begin{aligned}
\delta^2 E_{\text{xch}}^{(1)} &= \frac{1}{4} \iint \frac{1}{\|\mathbf{r} - \mathbf{r}'\|} \left(- \sum_{k=1}^n \sum_{\ell=1}^n \delta \rho_k^{(1)}(\mathbf{r}, \mathbf{r}') \delta \rho_{\ell}^{(1)}(\mathbf{r}, \mathbf{r}') \right. \\
&\quad - 2 \sum_{k=1}^m \sum_{\ell=1}^m \delta \rho_{k+n}^{(1)}(\mathbf{r}, \mathbf{r}') \delta \rho_{\ell}^{(1)}(\mathbf{r}, \mathbf{r}') \\
&\quad \left. + 2 \sum_{k=1}^m \sum_{\ell=1}^m g_{k,\ell} \delta \rho_{k+n}^{(1)}(\mathbf{r}, \mathbf{r}') \delta \rho_{\ell+n}^{(1)}(\mathbf{r}, \mathbf{r}') \right) d\mathbf{r} d\mathbf{r}' \quad (89)
\end{aligned}$$

Combining the expressions for the various relaxation energies, Eqs. (70), (71), (87) and (90), one obtains the following expression for the ASED energy through first-order

$$E_{\text{ASED}}^{(0+1)} = E_{\text{el}}^{\text{at}} + E_{\text{el}} + E_{\text{xch}}^0 + \delta E_{\text{ASED}}^{(0+1)} + \delta^2 E_{\text{ASED}}^{(0+1)} \quad (90)$$

Moreover, the energy term linear in the density-matrix relaxation can be written as the expectation value of Fock-type operators.

Combining Eqs. (70) and (86) one obtains

$$\begin{aligned}
\delta E_{\text{ASED}}^{(0+1)} &= \sum_{k=1}^n \int_{\mathbf{r}'=\mathbf{r}} \hat{F}_k^{\text{C}} \delta \rho_k^{(1)}(\mathbf{r}, \mathbf{r}') d\mathbf{r} \\
&\quad + \sum_{k=1}^m \int_{\mathbf{r}'=\mathbf{r}} \hat{F}_k^0 \delta \rho_{k+n}^{(1)}(\mathbf{r}, \mathbf{r}') d\mathbf{r} \quad (91)
\end{aligned}$$

where the Fock operators \hat{F}_k^{C} and \hat{F}_k^0 are

$$\hat{F}_k^{\text{C}} = \hat{h} + \sum_{\ell=1}^n (2\hat{j}_{\ell}^0 - \hat{K}_{\ell}^0) + \sum_{\ell=1}^m (\hat{j}_{\ell+n}^0 - \frac{1}{2} \hat{K}_{\ell+n}^0) \quad (92a)$$

$$\hat{F}_k^0 = \hat{h} + \sum_{\ell=1}^n (2\hat{j}_{\ell}^0 - \hat{K}_{\ell}^0) + \sum_{\ell=1}^m (\hat{j}_{\ell+n}^0 + g_{k\ell} \hat{K}_{\ell+n}^0) \quad (92b)$$

When the limit orbitals, $\{\psi_k^0\}$, are each just the atomic orbitals, as in the case of all heteronuclear molecules, the Coulomb and

exchange potentials may be grouped according to the atomic nucleus of the atomic orbitals from which the potentials are derived. In those cases, the Fock operators consist, apart from the kinetic energy operator, of superpositions of atomic effective potentials

$$\hat{F}^C = -\frac{1}{2}\nabla^2 + \sum_A \hat{V}_A^C \quad (93a)$$

$$\hat{F}_k^0 = -\frac{1}{2}\nabla^2 + \sum_A \hat{V}_{k,A}^0 \quad (93b)$$

where the atomic effective potentials are defined as

$$\hat{V}_A^C = -\frac{Z_A}{\|\mathbf{r} - \mathbf{R}_A\|} + \sum_{\ell \in S_A^C} (2\hat{j}_\ell^0 - \hat{K}_\ell^0) + \sum_{\ell \in S_A^0} (\hat{j}_{\ell+n}^0 - \frac{1}{2} \hat{K}_{\ell+n}^0) \quad (94a)$$

$$\hat{V}_{k,A}^0 = -\frac{Z_A}{\|\mathbf{r} - \mathbf{R}_A\|} + \sum_{\ell \in S_A^C} (2\hat{j}_\ell^0 - \hat{K}_\ell^0) + \sum_{\ell \in S_A^0} (\hat{j}_{\ell+n}^0 + g_{k,\ell} \hat{K}_{\ell+n}^0) \quad (94b)$$

The S_A^C and S_A^0 denote respectively the sets of integer labels of the doubly and singly occupied atomic orbitals of nuclear center A.

The net non-linear effect on the energy due to the relaxation in the density-matrix is obtained by combining Eqs. (71) and (89). One obtains

$$\begin{aligned} \delta^2 E_{ASED}^{(0+1)} = & \frac{1}{4} \iint \frac{1}{\|\mathbf{r} - \mathbf{r}'\|} \left[2\delta\rho^{(1)}(\mathbf{r})\delta\rho^{(1)}(\mathbf{r}') - \delta\rho^{(1)}(\mathbf{r},\mathbf{r}')\delta\rho^{(1)}(\mathbf{r},\mathbf{r}') \right. \\ & \left. + \sum_{k=1}^m \sum_{\ell=1}^m (2g_{k\ell} + 1) \delta\rho_{k+n}^{(1)}(\mathbf{r},\mathbf{r}')\delta\rho_{\ell+n}^{(1)}(\mathbf{r},\mathbf{r}') \right] d\mathbf{r} d\mathbf{r}' \quad (95) \end{aligned}$$

The correlation energy has been defined previously, Eq. (42), as

$$E_{el}^{corr.} = E_{el}^{(2)} + E_{el}^{(3)} + \dots \quad (96)$$

This perturbation expansion of the electronic energy follows along conventional lines⁽³²⁻³⁴⁾ from the definition of a partition of the electronic hamiltonian, Eqs. (34)-(36), and Eq. (38). The second-order Rayleigh-Schrödinger perturbation correction to the energy, for example, is

$$E_{el}^{(2)} = - \sum_k \sum_a |\langle \psi^{(0)} | \hat{H} | \psi_k^a \rangle|^2 / (\epsilon_a - \epsilon_k) \\ - \sum_{k>l} \sum_{a>b} |\langle \psi^{(0)} | \hat{H} | \psi_{k,l}^{a,b} \rangle|^2 / (\epsilon_a + \epsilon_b - \epsilon_l - \epsilon_k) \quad (97)$$

The ψ_k^a and $\psi_{k,l}^{a,b}$ are the configuration functions generated, respectively, by replacing one or two of the occupied orbitals (denoted by k, l, \dots) in the orbital product of the zero-order wavefunction $\psi^{(0)}$ with unoccupied orbitals (denoted by a, b, \dots). The second-order energy, $E_{el}^{(2)}$, has non-vanishing contributions from single-excitation configuration functions because the molecular orbitals used here do not satisfy the Brillouin condition.⁽⁴²⁾

This perturbation formulation is not directly applicable when an incorrect admixture of covalent and ionic terms in the wavefunction causes extraneous long-range terms to appear in the first-order energy. The terms in the correlation energy that cancel this extraneous long-range behavior derive, as is well known, from the configuration-functions involving excitations to those unoccupied molecular orbitals

that become degenerate with the occupied orbitals as the atoms separate. In order to continuously treat the correlation correction to the exchange energy, a prior transformation of the hamiltonian matrix has to be made that properly resolves the increasing degeneracy in the domain of large internuclear separations. One method applied to a variety of problems of this type is the Van Vleck transformation.⁽⁴³⁾ Consider the hamiltonian submatrix that derives from the subspace consisting of $\psi^{(0)}$ and all configuration functions generated by excitations to unoccupied orbitals that, as the atoms separate, become degenerate with the occupied orbitals. A straightforward application of the Van Vleck transformation modifies the coupling of the sub-matrix to the remaining matrix so that the modified off-diagonal coupling terms are reduced to be of second-order or higher in the perturbation. As is well known, the eigenvalues of the actual transformed sub-matrix are then automatically accurate through third-order in the perturbation expansion, since the modified off-diagonal coupling terms can only contribute to these energies in fourth-order or higher.

The correlation energy can also be obtained by the more traditional variational configuration interaction (CI) approach.⁽⁴⁴⁾ The standard CI variational energy is

$$E_{el} = \sum_i \sum_j c_i H_{ij} c_j \quad (98a)$$

where

$$H_{ij} = \langle \psi_i | \hat{H} | \psi_j \rangle \quad (98b)$$

and ψ_i stands for the i 'th configuration-function, and ψ_1 is defined as the zero-order wavefunction, $\psi^{(0)}$. Each diagonal hamiltonian matrix element can be decomposed as shown in Eq. (91). Note that the latter equation is just a prototype for all diagonal matrix-elements since

$$E_{e.l.}^{(0)} + E_{e.l.}^{(1)} = \langle \psi_1 | \hat{H} | \psi_1 \rangle \quad (99)$$

Each element, in general, has its own particular separated-atoms limit characteristics relative to which the relaxation terms are defined. Extending these arguments to the off-diagonal hamiltonian matrix elements, we write formally

$$H_{ii} = (E_{cl})_{ii} + (E_{cl}^{at})_{ii} + (E_{xch}^0)_{ii} + \delta H_{ii} + \delta^2 H_{ii} \quad (100a)$$

$$H_{ij} = H_{ij}^0 + \delta H_{ij} + \delta^2 H_{ij} \quad (100b)$$

where H_{ij}^0 is the off-diagonal element constructed from the limiting orbitals of the configuration functions ψ_i and ψ_j , and δH_{ij} and $\delta^2 H_{ij}$ are the relaxation effects relative to H_{ij}^0 .

IV. DISCUSSION

The molecular orbital energies, ϵ_k , obtained by solving the ASED one-electron equation, Eq. (44), become the atomic orbital energies in the limit as the atoms of the molecule are infinitely separated. The reason is that, in this limit, the ASED orbital equation describes a single electron in the field of the isolated atomic potentials. The resulting spectrum of one-electron states in this limit is, therefore, just the superposition of the one-electron states of each of the atomic potentials. This property enables one to follow in a continuous fashion the evolution of the ASED molecular orbital energy levels from their parent atomic levels. Moreover, in this limit the molecular orbitals, ψ_k , become either the atomic orbitals themselves, or, otherwise, just spatial-symmetry-dictated combinations of these atomic orbitals.

The ASED zero-order energy, Eq. (45), is determined by occupying the molecular orbital levels resulting from Eq. (44) in order of increasing energy, ϵ_k , according to the usual building-up principles. This choice of the orbital occupation may not always lead to the desired diabatic electronic state at all internuclear separations. A different orbital occupation may be characteristic of the adiabatic state in these other domains of the energy surface. In these cases it clearly becomes necessary to go beyond the ASED energy through first-order, Eq. (91), to a configuration interaction (CI) calculation of the energy. The configuration functions are the various zero-order wavefunctions, Eq. (46), corresponding to the different choices of orbital occupation. Despite

the increased complexity, the ASED energy decomposition scheme can still be used even in this case to simplify the CI energy calculation.

A. The LiH molecule

To illustrate the above, we consider formal aspects of the ASED application to the LiH molecule in the $\chi^1\Sigma^+$ state. The molecular orbitals obtained by solving Eq. (44), $\{1\sigma, 2\sigma, 3\sigma, 4\sigma, \dots\}$, approach the limits

$$1\sigma \longrightarrow 1s_{\text{Li}} \quad (101a)$$

$$2\sigma \longrightarrow 1s_{\text{H}} \quad (101b)$$

$$3\sigma \longrightarrow 2s_{\text{Li}} \quad (101c)$$

$$4\sigma \longrightarrow 2p\sigma_{\text{Li}} \quad (101d)$$

.....

as the Li and H atoms separate. The application of the building-up principle leads to the following ASED zero-order wavefunction

$$\psi_1^{(0)} = A (1\sigma^2 2\sigma^2 \alpha\beta \alpha\beta) \quad (102)$$

As the atoms separate, this wavefunction approaches the $\text{Li}^+ (1s) + \text{H}^- (1s)$ limit. The one-electron density matrix deriving from $\psi_1^{(0)}$ is

$$\rho^{(1)}(r, r') = 2(1\sigma \cdot 1\sigma) + 2(2\sigma \cdot 2\sigma) \quad (103a)$$

At large internuclear distances, $\rho^{(1)}(r, r')$ approaches the superposition of atomic-ions density matrices

$$\rho^{\text{sup}}(r, r') = 2(1s_{\text{Li}} \cdot 1s_{\text{Li}}) + 2(1s_{\text{H}} \cdot 1s_{\text{H}}) \quad (103b)$$

We adopt here the convention of using a dot between each pair of orbitals in the expansion of the density matrix to indicate that they depend separately on the spatial coordinates r and r' . In contrast the adiabatic electronic $X^1\Sigma^+$ state approaches the neutral atom limit $\text{Li}(^2S) + \text{H}(^2S)$ at large internuclear separations. The ASED zero-order wavefunction describing this limit is

$$\psi_2^{(0)} = A \left(1\sigma^2 \ 2\sigma 3\sigma \ \alpha\beta \frac{(\alpha\beta - \beta\alpha)}{\sqrt{2}} \right) \quad (104)$$

with obviously different orbital occupations than obtained by application of the building-up principle. The one-electron density matrix deriving from $\psi_2^{(0)}$ is

$$\rho^{(1)}(r, r') = 2(1\sigma \cdot 1\sigma) + 2\sigma \cdot 2\sigma + 3\sigma \cdot 3\sigma \quad (105a)$$

At large internuclear distances, $\rho^{(1)}(r, r')$ approaches the superposition of neutral atom density matrices

$$\rho^{\text{sup}}(r, r') = 2(1s_{\text{Li}} \cdot 1s_{\text{Li}}) + 2s_{\text{Li}} \cdot 2s_{\text{Li}} + 1s_{\text{H}} \cdot 1s_{\text{H}} \quad (105b)$$

The CI wavefunction is a linear combination of the two alternative zero-order wavefunctions, Eqs. (102) and (104). The diagonal elements of the hamiltonian matrix in this configuration function space are the same as the energies through first-order for each zero-order wavefunction separately. The ASED decomposition for each diagonal hamiltonian matrix element is obtained in Eq. (100a).

Whereas the ASED decomposition for the H_{22} element is based on the superposition of neutral atoms in the first stage of bonding, the ASED decomposition of the H_{11} element is based instead on the superposition of atomic ions. Thus, at large internuclear separations, D.

$$\left(E_{cl}\right)_{11} \sim -\frac{1}{D} \quad (106)$$

while $(E_{cl})_{22}$ just falls off exponentially to zero. The detailed formulae for $(E_{cl})_{ii}$, $(E_{cl}^{at})_{ii}$, $(E_{xch}^0)_{ii}$ are special cases, respectively, of Eqs. (28), (72) and (77). We divide $(E_{xch}^0)_{ii}$ into those terms that are atomic exchange energies, and hence remain constant, and those terms that vary with internuclear separation. We write

$$\left(E_{xch}^0\right)_{ii} = \left(E_{xch}^{at}\right)_{ii} + \left(\Delta E_{xch}^0\right)_{ii} \quad (107)$$

In the present example, these terms are

$$\left(E_{xch}^{at}\right)_{11} = -K_{1s_{Li},1s_{Li}} - K_{1s_H,1s_H} \quad (108a)$$

$$\left(\Delta E_{xch}^0\right)_{11} = -2 K_{1s_H,1s_{Li}} \quad (108b)$$

and

$$\begin{aligned} \left(E_{xch}^{at}\right)_{22} &= -K_{1s_{Li},1s_{Li}} - K_{1s_{Li},2s_{Li}} \\ &\quad - \frac{1}{2} K_{2s_{Li},2s_{Li}} - \frac{1}{2} K_{1s_H,1s_H} \end{aligned} \quad (108c)$$

$$\left(\Delta E_{xch}^0\right)_{22} = -K_{1s_H,1s_{Li}} + K_{1s_H,2s_{Li}} \quad (108d)$$

The general formulae giving the effects on the energy of relaxations in the one-electron density matrix are Eqs. (92), (93) and (96). For purposes of illustration, we next give just the linear relaxation terms for this case. First, relative to the superposition of atomic-ion density matrices, one obtains

$$\delta H_{11} = 2 \langle 1\sigma - 1s_{Li} | \hat{F}^C | 1\sigma + 1s_{Li} \rangle + 2 \langle 2\sigma - 1s_H | \hat{F}^C | 2\sigma + 1s_H \rangle \quad (109a)$$

where

$$\hat{F}^C = \hat{h} + \left(2\hat{J}_{1s_{Li}} - \hat{K}_{1s_{Li}} \right) + \left(2\hat{J}_{1s_H} - \hat{K}_{1s_H} \right) \quad (109b)$$

Second, relative to the superposition of neutral-atom density matrices, one obtains

$$\begin{aligned} \delta H_{22} = & 2 \langle 1\sigma - 1s_{Li} | \hat{F}^C | 1\sigma + 1s_{Li} \rangle + \langle 2\sigma - 1s_H | \hat{F}_{2\sigma}^0 | 2\sigma + 1s_H \rangle \\ & + \langle 3\sigma - 2s_{Li} | \hat{F}_{3\sigma}^0 | 3\sigma + 2s_{Li} \rangle \end{aligned} \quad (110a)$$

where

$$\begin{aligned} \hat{F}^C = & \hat{h} + \left(2\hat{J}_{1s_{Li}} - \hat{K}_{1s_{Li}} \right) + \left(\hat{J}_{2s_{Li}} - \frac{1}{2} \hat{K}_{2s_{Li}} \right) \\ & + \left(\hat{J}_{1s_H} - \frac{1}{2} \hat{K}_{1s_H} \right) \end{aligned} \quad (110b)$$

$$\begin{aligned} \hat{F}_{2\sigma}^0 = & \hat{h} + \left(2\hat{J}_{1s_{Li}} - \hat{K}_{1s_{Li}} \right) + \left(\hat{J}_{2s_{Li}} + \hat{K}_{2s_{Li}} \right) \\ & + \left(\hat{J}_{1s_H} - \hat{K}_{1s_H} \right) \end{aligned} \quad (110c)$$

$$\begin{aligned} \hat{F}_{3\sigma}^0 = & \hat{h} + \left(2\hat{J}_{1s_{Li}} - \hat{K}_{1s_{Li}} \right) + \left(\hat{J}_{2s_{Li}} - \hat{K}_{2s_{Li}} \right) \\ & + \left(\hat{J}_{1s_H} + \hat{K}_{1s_H} \right) \end{aligned} \quad (110d)$$

Both the $(\Delta E_{xch}^0)_{ij}$ and δH_{ij} terms are seen to fall off exponentially to zero at large internuclear separations. The long-range interactions, if present, are carried by the $(E_{el})_{ij}$ terms. The net limiting values of H_{ij} at the separated-atoms limit is given by combining $(E_{el}^{at})_{ij}$ with $(E_{xch}^{at})_{ij}$ one obtains

$$(E_{el}^{at} + E_{xch}^{at})_{11} = E_{Li^+} + E_{H^-} \quad (111a)$$

and

$$(E_{el}^{at} + E_{xch}^{at})_{22} = E_{Li} + E_H \quad (111b)$$

E_{Li^+} and E_{H^-} are the Li^+ and H^- ion energies in the Hartree-Fock approximation,

$$E_{Li^+} = 2\langle 1s_{Li} | \hat{h}_{Li} | 1s_{Li} \rangle + \left(2J_{1s_{Li}, 1s_{Li}} - K_{1s_{Li}, 1s_{Li}} \right) \quad (112a)$$

$$E_{H^-} = 2\langle 1s_H | \hat{h}_H | 1s_H \rangle + J_{1s_H, 1s_H} \quad (112b)$$

E_{Li} and E_H are the analogous energies for the Li and H atoms,

$$E_{Li} = E_{Li^+} + \langle 2s_{Li} | \hat{h}_{Li} | 2s_{Li} \rangle + \left(2J_{1s_{Li}, 2s_{Li}} - K_{1s_{Li}, 2s_{Li}} \right) \quad (113a)$$

$$E_H = \langle 1s_H | \hat{h}_H | 1s_H \rangle \quad (113b)$$

In these equations \hat{h}_{Li} and \hat{h}_H are the one-electron operators, Eq. 31b), for the Li and H atom cases respectively.

The off-diagonal hamiltonian matrix element is folded into a form analogous to that obtained for the diagonal elements as indicated in Eq. (100b).

The first term of Eq. (100b) in this case is

$$H_{12}^0 = \sqrt{2} \langle 2s_{Li} | \hat{F}^C | 1s_H \rangle \quad (114a)$$

where

$$\hat{F}^C = \hat{h} + \left(2\hat{J}_{1s_{Li}} - \hat{K}_{1s_{Li}} \right) + \hat{J}_{1s_H} \quad (114b)$$

In relaxation terms are

$$\begin{aligned} \delta H_{12} = \sqrt{2} & \left(\int_{\chi^i=r} \hat{F}^C \delta\rho_{2\sigma,3\sigma}^{(1)}(\chi, \chi') d\chi \right. \\ & + \int_{\chi^i=\chi} \left(\hat{J}_{1s_H,2s_{Li}} - \frac{1}{2} \hat{K}_{1s_H,2s_{Li}} \right) \delta\rho_{1\sigma}^{(1)}(\chi, \chi') d\chi \\ & \left. + \int \hat{J}_{1s_H,2s_{Li}} \delta\rho_{2\sigma}^{(1)}(\chi) d\chi \right) \quad (115a) \end{aligned}$$

and

$$\begin{aligned} \delta^2 H_{12} = \sqrt{2} & \iint \frac{1}{\|\chi - \chi'\|} \left[\delta\rho_{2\sigma,3\sigma}^{(1)}(\chi) \left(\delta\rho_{1\sigma}^{(1)}(\chi') \right. \right. \\ & \left. \left. + \delta\rho_{2\sigma}^{(1)}(\chi') \right) - \frac{1}{2} \delta\rho_{2\sigma,3\sigma}^{(1)}(\chi, \chi') \delta\rho_{1\sigma}^{(1)}(\chi, \chi') \right] d\chi d\chi' \quad (115b) \end{aligned}$$

where

$$\delta\rho_{2\sigma,3\sigma}^{(1)}(\chi, \chi') = 2\sigma.3\sigma - 1s_H.2s_{Li} \quad (116a)$$

$$\delta\rho_{1\sigma}^{(1)}(\chi, \chi') = 2 (1\sigma.1\sigma - 1s_{Li}.1s_{Li}) \quad (116b)$$

$$\delta\rho_{2\sigma}^{(1)}(\chi) = 2\sigma.2\sigma - 1s_H.1s_H \quad (116c)$$

B. The H_2 molecule

A prototype case illustrating a quite different challenge for the ASED energy decomposition is found in the H_2 molecule in the $\chi^1 \Sigma_g^+$ state. The ASED orbital equation in this case is the same as that of the H_2^+ molecule-ion problem. The molecular orbitals obtained from solving the equation, $\{1\sigma_g, 1\sigma_u, \dots\}$, approach the limits

$$1\sigma_g \longrightarrow \frac{1}{\sqrt{2}} (1s_A + 1s_B) \quad (117a)$$

$$1\sigma_u \longrightarrow \frac{1}{\sqrt{2}} (1s_A - 1s_B) \quad (117b)$$

as the H atoms separate. The two hydrogen atom orbitals are labeled $1s_A$ and $1s_B$. The ASED orbital energies, however, both approach the hydrogen atom orbital energy, ϵ_{1s} , as the atoms separate

$$\epsilon_{1\sigma_g} \longrightarrow \epsilon_{1s} \quad (118a)$$

$$\epsilon_{1\sigma_u} \longrightarrow \epsilon_{1s} \quad (118b)$$

The application of the building-up principle leads to the following ASED zero-order wavefunction

$$\psi^{(0)} = A (1\sigma_g)^2_{\alpha\beta} \quad (119)$$

The zero-order energy is

$$E_{el}^{(0)} = 2 \epsilon_{1\sigma_g} \quad (120)$$

It follows that the zero-order energy approaches the correct limiting energy as the atoms separate.

However, at large internuclear separations, the zero-order wavefunction, Eqn. (119a), becomes

$$\psi^{(0)} \longrightarrow A \left[\left(1s_A 1s_B + 1s_B 1s_A \right) \alpha\beta \right] + \Lambda \left[\left(1s_A^2 + 1s_B^2 \right) \alpha\beta \right]$$

The first component correctly describes the $H(2s) + H(2s)$ limit. The second component of this wavefunction, however, describes an ionic limit. This admixture of the covalent and ionic wavefunctions even in the separated-atoms limit is the cause of extraneous long-range terms in the first-order ASED energy to be discussed later.

The zero-order ASED energy is defined as

$$E_{\text{ASED}}^{(0)} = E_{cl} + E_{el}^{(0)} \quad (121)$$

The two components of $E_{\text{ASED}}^{(0)}$ superficially resemble the E_R and E_{EH} components of the energy *ansatz* in Anderson's semi-empirical ASED method, Eq. (6). Figure 3 shows that E_{cl} , except for a small attractive region, is mostly a repulsive energy curve. Figure 3 also shows that $\Delta E_{el}^{(0)}$, in contrast to E_{cl} , is a strongly attractive energy curve. The nature of these curves is consistent with Anderson's qualitative arguments.⁽¹³⁾ In these calculations we have used the approximation of restricting the orbitals to a minimum basis set in order to simplify the calculations.⁽⁴⁵⁾ The net energy curve, $\Delta E_{\text{ASED}}^{(0)}$, is also shown in Fig. 3 together, for reference purposes, with the exact potential energy curve.⁽⁴⁶⁾ This comparison shows that the zero-order ASED energy is quantitatively in gross error. The binding energy is overestimated by an order of magnitude.

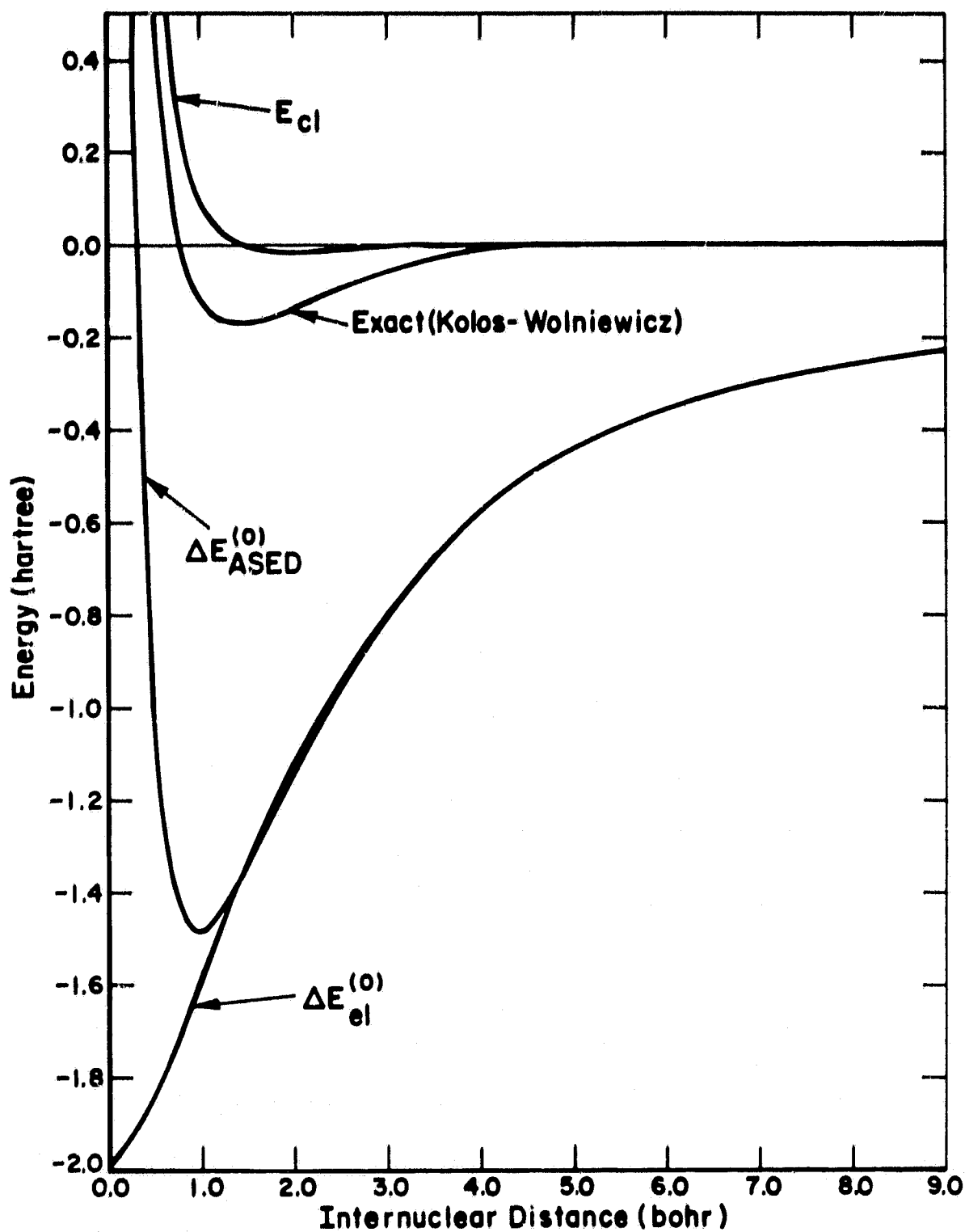


FIG. 3. The zero-order electronic energy $\Delta E_{el}^{(0)}$, the classical electrostatic energy E_{cl} , and the net ASE zero-order potential energy, $\Delta E_{ASED}^{(0)}$, as a function of internuclear distance for the H_2 molecule in the $X^1\Sigma_g^+$ state. The exact potential energy curve⁽⁴⁶⁾ is also shown for purposes of comparison.

The first-order ASED energy is defined as

$$E_{\text{ASED}}^{(0+1)} = E_{el}^{\text{at}} + E_{cl} + \delta E_{el}^{(0+1)} + \delta^2 E_{el}^{(0+1)} + F^{(0+1)} \quad (122)$$

The linear relaxation energy is divided into contributions from the kinetic, electron-nucleus, and electron-electron repulsion energy

$$\delta E_{el}^{(0+1)} = \delta E_{kin}^{(0+1)} + \delta E_{en}^{(0+1)} + \delta E_{ee}^{(0+1)} \quad (123)$$

The various relaxation energies are defined as

$$E_{kin}^{(0+1)} = \int_{\mathcal{R}} \left(-\frac{1}{2\nabla^2} \right) \delta \rho^{(1)}(\mathcal{R}, \mathcal{R}') d\mathcal{R} \quad (124a)$$

$$\delta E_{en}^{(0+1)} = \int \left(\frac{-1}{\|\mathcal{R} - \mathcal{R}_A\|} + \frac{-1}{\|\mathcal{R} - \mathcal{R}_B\|} \right) \delta \rho^{(1)}(\mathcal{R}) d\mathcal{R} \quad (124b)$$

$$\delta E_{ee}^{(0+1)} = \frac{1}{2} \iint \frac{1}{\|\mathcal{R} - \mathcal{R}'\|} \rho^{\text{sup}}(\mathcal{R}) \delta^{(1)}(\mathcal{R}') d\mathcal{R} d\mathcal{R}' \quad (124c)$$

where the relaxation in the one-electron density matrix is

$$\delta \rho^{(1)}(\mathcal{R}, \mathcal{R}') = 2(1\sigma_g \ 1\sigma_g) - \rho^{\text{sup}}(\mathcal{R}, \mathcal{R}') \quad (125a)$$

$$\rho^{\text{sup}}(\mathcal{R}, \mathcal{R}') = 1s_A \cdot 1s_A + 1s_B \cdot 1s_B \quad (125b)$$

The non-linear effect on the energy due to the relaxation in the electron density is

$$\delta^2 E_{el}^{(0+1)} = \frac{1}{4} \iint \frac{1}{\|\mathcal{R} - \mathcal{R}'\|} \delta \rho^{(1)}(\mathcal{R}) \delta \rho^{(1)}(\mathcal{R}') d\mathcal{R} d\mathcal{R}' \quad (126)$$

Note that we have dispensed with the division of the electron-electron repulsion energy into a coulomb and an exchange contribution. As is well known, in this case, the first-order energy contains terms that cause this energy to approach the wrong limit as the atoms separate.⁽⁴⁷⁾ The partition of the electron-electron repulsion energy only

serves to obscure the problem in this case. The terms in the ASED energy, Eq. (122b), that cause this incorrect approach to the limit are isolated in the $F^{(0+1)}$ term. This term is

$$F^{(0+1)} = \frac{1}{2} \left(J_{1s_A, 1s_A} - J_{1s_A, 1s_B} \right) \quad (127)$$

with the property that, at large internuclear distances, D , it behaves as

$$F^{(0+1)} \sim \frac{1}{2} \left(J_{1s_A, 1s_A} - \frac{1}{D} \right) \quad (128)$$

The first term in Eq. (122), E_{el}^{at} , contains the correct separated-atoms limit energy, namely

$$E_{el}^{at} = 2\varepsilon_{1s} \quad (129)$$

The various relaxation energies are shown in Fig. 4 as a function of internuclear distance. This figure shows that the relaxation effects in the kinetic energy and the electron-nuclear attraction energy, $\delta E_{kin}^{(0+1)}$ and $\delta E_{en}^{(0+1)}$ respectively, are by far the dominant contributions to the total relaxation energy. The linear relaxation effect in the electron-electron repulsion energy, $E_{ee}^{(0+1)}$ is shown in Fig. 4 to be a comparatively small and slowly varying. The non-linear relaxation effect, $\delta^2 E_{ee}^{(0+1)}$, is shown in Fig. 4 to be negligibly small.

The total linear relaxation energy, $\delta E_{el}^{(0+1)}$, and the classical electrostatic energy, E_{cl} , are shown in Fig. 5 as a function of internuclear distance. As already seen on Fig. 3, E_{cl} does have a small attractive region. The linear relaxation energy, however, is the dominant attractive energy contribution. At small internuclear distances,

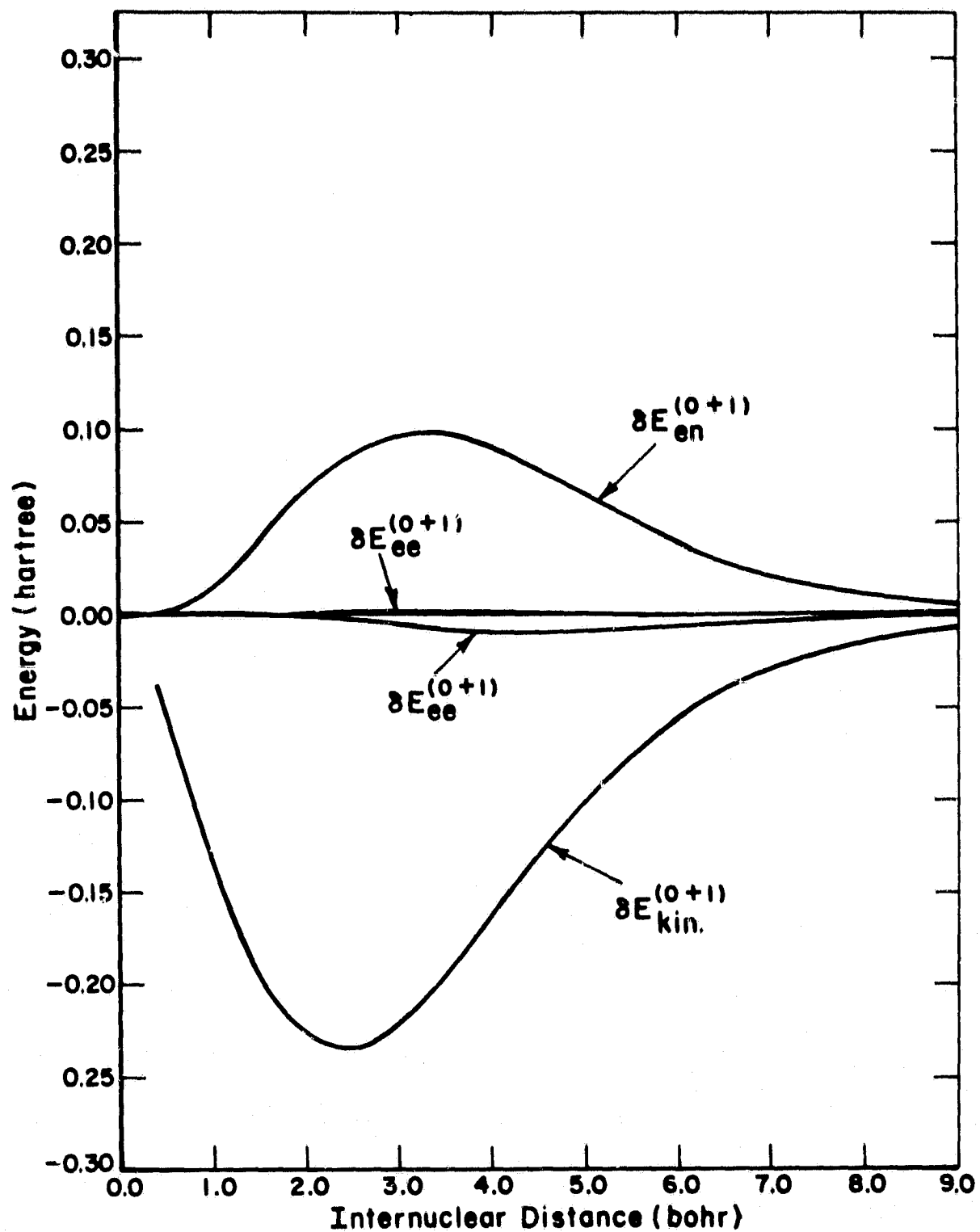


FIG. 4. The relaxation in the various components of the electronic energy as a function of internuclear distance, for the H_2 molecule in the $X^1\Sigma_g^+$ state.

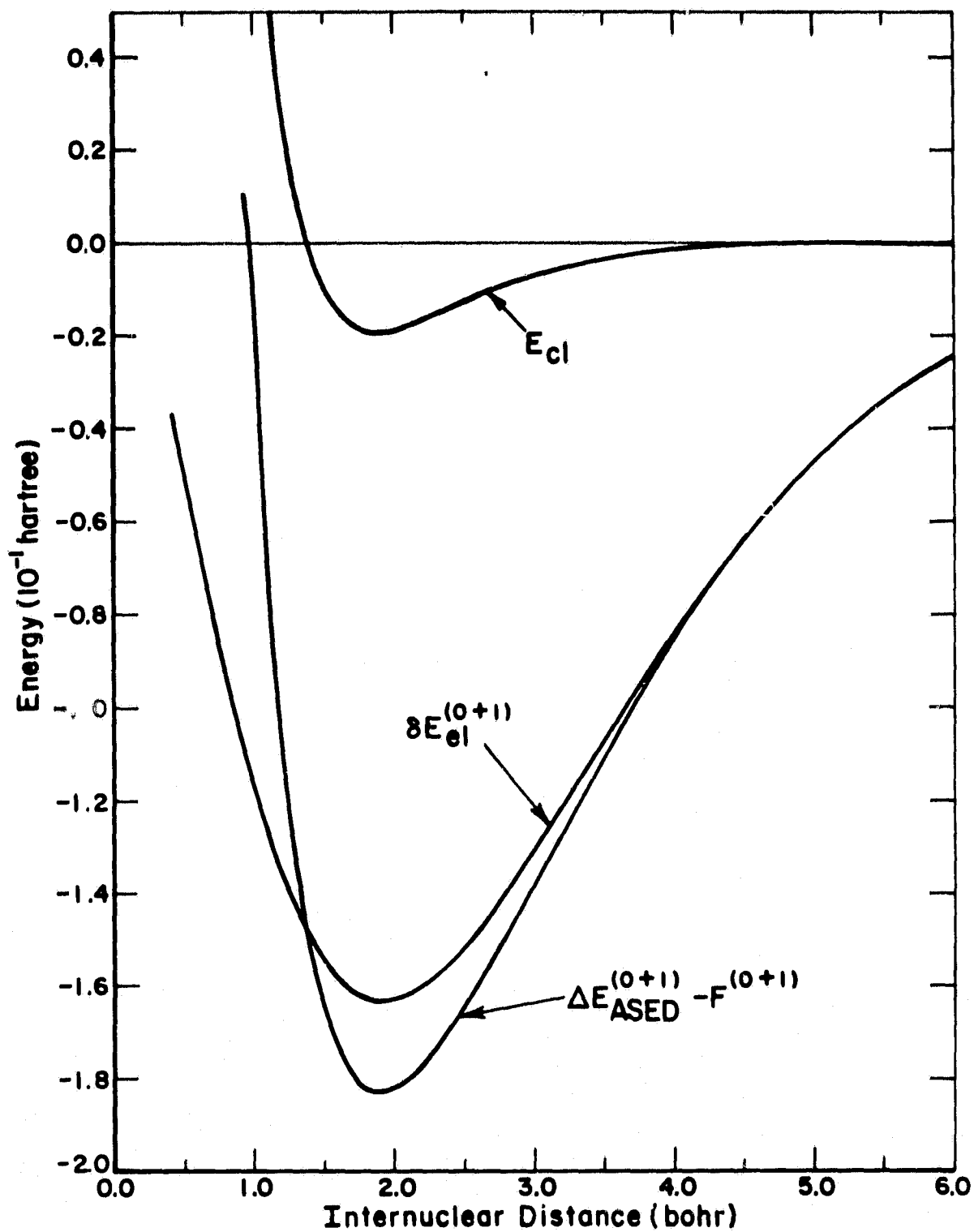


FIG. 5. Decomposition of the partial ASED energy through first-order, $\Delta E_{ASED}^{(0+1)} - F^{(0+1)}$, into the classical electrostatic energy, E_{cl} , and the relaxation energy, $\delta E_{el}^{(0+1)}$, for the H_2 molecule in the $X^1\Sigma_g^+$ state.

the repulsive energy is derived dominantly from $E_{c\ell}$. The $F^{(0+1)}$ term is not by itself a meaningful term. We show later that there are terms in the correlation energy that precisely match this term, and that, when combined with $F^{(0+1)}$ yield a net meaningful interaction. For this reason, we only show a part of the first-order ASED energy in Fig. 5, namely $(\Delta E_{\text{ASED}}^{(0+1)} - F^{(0+1)})$. This partial energy is in fact just the sum of $E_{c\ell}$ and $\delta E_{c\ell}^{(0+1)}$. The Δ in the notation $\Delta E_{\text{ASED}}^{(0+1)}$ indicates that the energy of the separated atom, $E_{c\ell}^{\text{at}}$, has been subtracted from $E_{\text{ASED}}^{(0+1)}$. Figure 6 shows an alternative interesting decomposition of the partial energy $(\Delta E_{\text{ASED}}^{(0+1)} - F^{(0+1)})$. In this figure we show that, when $\delta E_{e\ell}^{(0+1)}$ and $\delta E_{ee}^{(0+1)}$ are combined with $E_{c\ell}$, a purely repulsive electrostatic type of energy is obtained. This decomposition focuses attention on the relaxation in the kinetic energy, $\delta E_{\text{kin}}^{(0+1)}$, as source of the attractive energy leading to chemical binding.^(19,20,48) Figure 7 shows a comparison of the partial first-order ASED energy curve with the exact energy curve⁽⁴⁶⁾ and the Hartree-Fock energy curve.⁽⁴⁷⁾ We note that there is a considerable improvement in the comparison with the exact result in going from the zero-order curves, Fig. 3, to the present one. The binding energy, for example, is now within 5% of the exact result instead of being off by an order of magnitude. Detailed properties of the partial first-order energy alone, however, are not in good agreement. The equilibrium bond length is overestimated by about 0.5 bohr, and the range of significant binding extends to internuclear distances that are much too large. The Hartree-Fock energy, E_{HF} , is shown in Fig. 7 for comparison purposes in the form of a "rationalized" potential energy curve,⁽⁴⁹⁾ namely

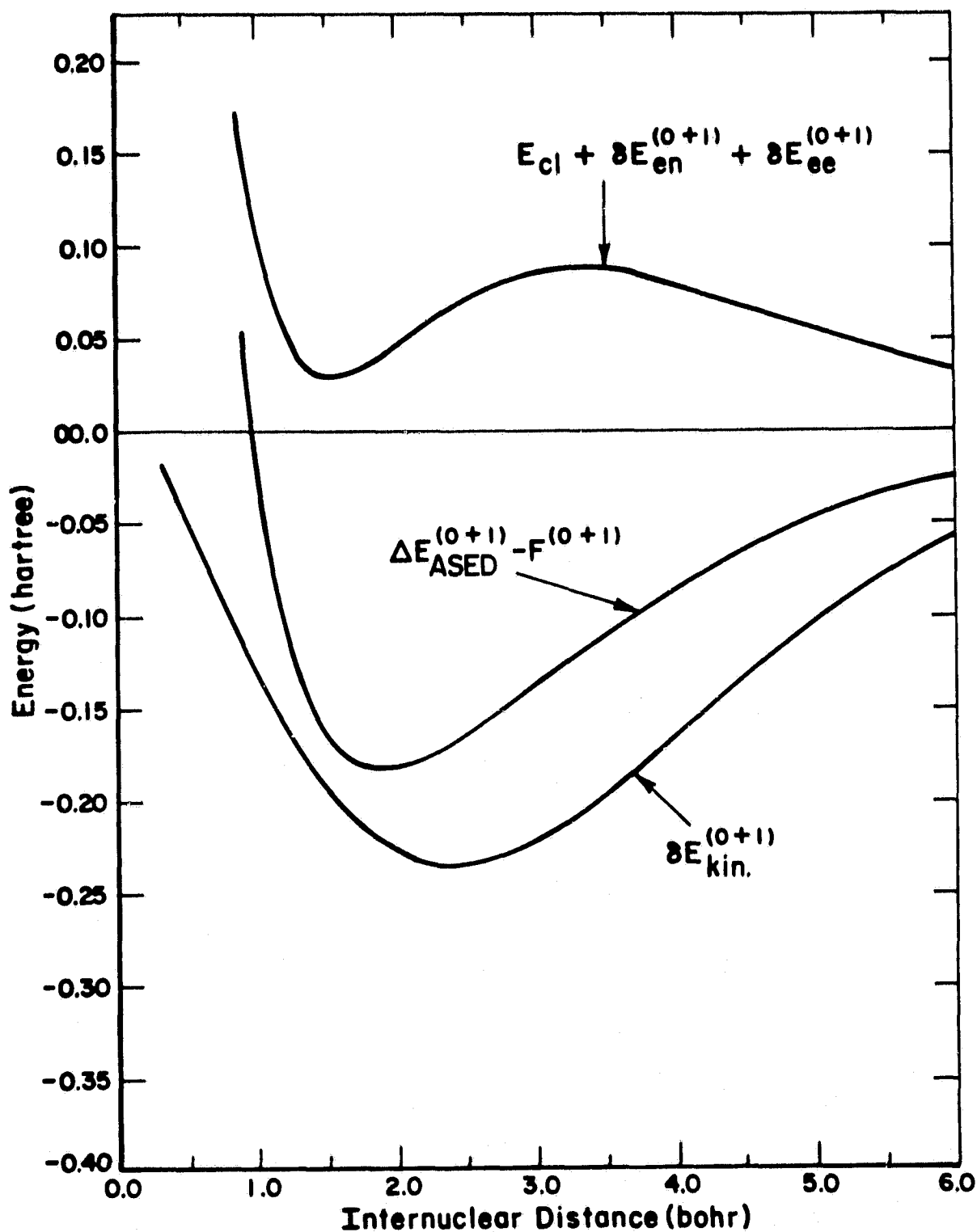


FIG. 6. Decomposition of the partial ASED energy through first-order, $\Delta E_{ASED}^{(0+1)} - F^{(0+1)}$, into an effective electrostatic energy, $E_{cl} + \delta E_{en}^{(0+1)} + \delta E_{ee}^{(0+1)}$, and the relaxation in the kinetic energy, $\delta E_{kin}^{(0+1)}$, for the H_2 molecule in the $X^1\Sigma_g^+$ state.

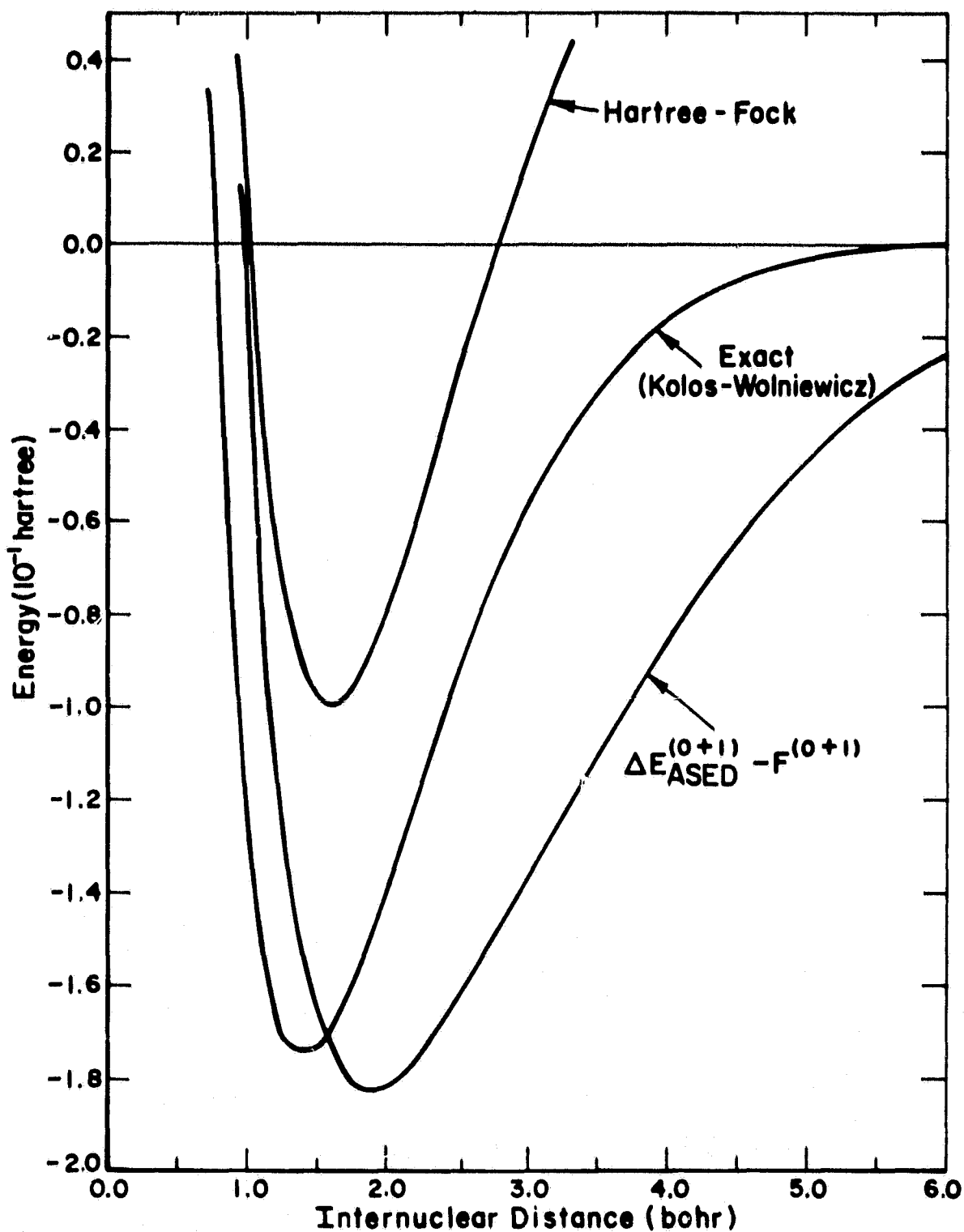


FIG. 7. Comparison of the partial ASED energy through first-order, $\Delta E_{\text{ASED}}^{(0+1)} - F^{(0+1)}$, with the Hartree-Fock⁽⁴⁷⁾ and the exact⁽⁴⁶⁾ potential energy curves, for the H_2 molecule in the $X^1 \Sigma_g^+$ state.

$$\Delta E_{\text{HF}} = E_{\text{HF}} - E_{\text{el}}^{\text{at}} \quad (130)$$

The first-order ASED potential energy curve is equal to this "rationalized" Hartree-Fock potential energy curve, i.e.

$$\Delta E_{\text{ASED}}^{(0+1)} = \Delta E_{\text{HF}} \quad (131)$$

except for negligible second-order effects. It appears from Fig. 7 that either ΔE_{HF} or $(\Delta E_{\text{ASED}} - F^{(0+1)})$ are equally unsatisfactory by themselves.

As alluded to previously, the $F^{(0+1)}$ term has a direct counterpart among the terms in the correlation energy. Let us consider the configuration interaction (CI) approach to the calculation of the correlation energy.^(47,50) The configuration functions⁽⁵⁰⁾ are

$$\psi_1 = A(1\sigma_g^2 \alpha\beta) \quad (132)$$

and

$$\psi_2 = A(1\sigma_u^2 \alpha\beta) \quad (133)$$

where ψ_1 is just the zero-order wavefunction, Eq. (119a), and the $1\sigma_u$ orbital in ψ_2 is the unoccupied solution of Eq. (44). The total CI wavefunction is

$$\psi = C_1 \psi_1 + C_2 \psi_2 \quad (134)$$

and the corresponding variational energy is

$$E_{\text{el}} = \begin{pmatrix} C_1 & C_2 \end{pmatrix} \begin{pmatrix} H_{11} & H_{12} \\ H_{12} & H_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} \quad (135)$$

The hamiltonian matrix elements can each be partitioned as we have already indicated in Eq. (100). The ASED molecular total energy, Eq. (29), is then obtained as

$$E_{\text{ASED}}^{\text{CI}} = E_{\text{el}}^{\text{at}} + E_{\text{el}} + \begin{pmatrix} c_1 & c_2 \end{pmatrix} \begin{pmatrix} \delta H_{11} & F^{(0+1)} + \delta H_{12} \\ F^{(0+1)} + \delta H_{12} & \delta H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} + F^{(0+1)} + \delta^2 E_{\text{el}}^{\text{CI}} \quad (136)$$

where $\delta^2 E$ contains all effects that are second-order in the relaxation of the appropriate one-electron density matrices. The relaxation matrix elements, δH_{ij} , are divided again into contributions from the kinetic, electron-nuclear attraction, and electron-electron repulsion energy,

$$\delta H_{ii} = \left(\delta H_{ii} \right)_{\text{kin}} + \left(\delta H_{ii} \right)_{\text{en}} + \left(\delta H_{ii} \right)_{\text{ee}} \quad (137)$$

$$\delta H_{ij} = \left(\delta H_{ij} \right)_{\text{ee}} \quad (138)$$

These three types of terms are defined as

$$\left(\delta H_{ii} \right)_{\text{kin}} = \int_{\chi=\chi'} \left(-\frac{1}{2} \nabla^2 \right) \delta \rho_{ii}^{(1)}(\chi, \chi') d\chi \quad (139a)$$

$$\left(\delta H_{ii} \right)_{\text{en}} = \iint \left(\frac{-1}{\|\chi - R_A\|} + \frac{-1}{\|\chi - R_B\|} \right) \delta \rho_{ii}^{(1)}(\chi) d\chi \quad (139b)$$

$$\left(\delta H_{ij}\right)_{ee} = \frac{1}{2} \iint \frac{1}{\|\chi - \chi'\|} \rho_{ij}^{\text{sup}}(\chi) \delta \rho_{ij}^{(1)}(\chi') d\chi d\chi' \quad (139c)$$

The relaxation in the density matrices of each CI matrix element is defined as follows:

$$\delta \rho_{11}^{(1)}(\chi, \chi') = 2(\langle 1\sigma_g | 1\sigma_g \rangle - \rho^{\text{sup}}(\chi, \chi')) \quad (140a)$$

$$\delta \rho_{22}^{(1)}(\chi, \chi') = 2(\langle 1\sigma_u | 1\sigma_u \rangle - \rho^{\text{sup}}(\chi, \chi')) \quad (140b)$$

$$\delta \rho_{12}^{(1)}(\chi, \chi') = 2(\langle 1\sigma_g | 1\sigma_u \rangle - \rho_{12}^{\text{sup}}(\chi, \chi')) \quad (140c)$$

and the superposition density matrices in this case are

$$\rho_{ii}^{\text{sup}}(\chi, \chi') = \rho^{\text{sup}}(\chi, \chi') \quad (141a)$$

$$\rho_{12}^{\text{sup}}(\chi, \chi') = \langle 1s_A | 1s_A \rangle - \langle 1s_B | 1s_B \rangle \quad (141b)$$

We note that, the same as for $(E_{el}^{(0)} + E_{el}^{(1)})$, Eqs. (90)-(94), the relaxation matrix-elements, Eqs. (138) and (139), are clearly integrals of just atomic operators acting on relaxation density matrices.

The molecular total energy, Eq. (137), can thus be written as

$$E_{\text{ASED}}^{\text{CI}} = E_{el}^{\text{at}} + E_{el} + \left(F^{(0+1)} + F^{(\text{corr})} \right) + \delta E_{el}^{\text{CI}} + \delta^2 E_{el}^{\text{CI}} \quad (142)$$

where the correlated linear relaxation energy is

$$\delta E_{el}^{\text{CI}} = E_{kin}^{\text{CI}} + \delta E_{en}^{\text{CI}} + \delta E_{ee}^{\text{CI}} \quad (143)$$

The individual types of energy contributing to the linear relaxation energy are

$$\delta E_{kin}^{\text{CI}} = \int_{\chi=\chi'} \left(-\frac{1}{2} \nabla^2 \right) \delta \rho_{\text{CI}}^{(1)}(\chi, \chi') d\chi \quad (144a)$$

$$\delta E_{en}^{CI} = \int \left(-\frac{1}{\|x - R_A\|} - \frac{1}{\|x - R_B\|} \right) \delta \rho_{CI}^{(1)}(x) dx \quad (144b)$$

$$\delta E_{ec}^{CI} = \frac{1}{2} \iint \frac{1}{\|x - x'\|} \left[\rho^{sup}(x) \delta \rho_{CI}^{(1)}(x') + \rho_{12}^{sup}(x) \left(2 C_1 \delta \rho_{12}^{(1)}(x') C_2 \right) \right] dx dx' \quad (144c)$$

where the relaxation in the CI one-electron density-matrix is defined as

$$\delta \rho_{CI}^{(1)}(x, x') = \rho_{CI}^{(1)}(x, x') - \rho^{sup}(x, x') \quad (145a)$$

and

$$\rho_{CI}^{(1)}(x, x') = C_1^2 \left(2 1_{\sigma_g} \cdot 1_{\sigma_g} \right) + C_2^2 \left(2 1_{\sigma_u} \cdot 1_{\sigma_u} \right). \quad (145b)$$

Also,

$$F^{(corr)} = 2 C_1 F^{(0+1)} C_2 \quad (146)$$

The CI coefficients C_1 and C_2 are the components of the eigenvectors of the secular equation that follows from Eq. (137). Neglecting non-linear relaxation effects, these CI coefficients are given by

$$C_1 = \left(F^{(0+1)} + \delta H_{12} \right) / \sqrt{(\delta H_{11} - \Lambda)^2 + (F^{(0+1)} + \delta H_{12})^2} \quad (147a)$$

$$C_2 = - \left(\delta H_{11} - \Lambda \right) / \sqrt{(\delta H_{11} - \Lambda)^2 + (F^{(0+1)} + \delta H_{12})^2} \quad (147b)$$

and the CI eigenvalues are given by

$$\Lambda = \frac{1}{2} \left(\delta H_{11} + \delta H_{22} \right) \pm \sqrt{\frac{1}{2} (\delta H_{11} - \delta H_{22})^2 + (F^{(0+1)} + \delta H_{12})^2}. \quad (148)$$

As the separated-atoms limit is approached, the CI coefficients of the lowest energy root approach the limits

$$c_1 \longrightarrow \frac{1}{\sqrt{2}} \quad (149a)$$

$$c_2 \longrightarrow \frac{-1}{\sqrt{2}} \quad (149b)$$

and, hence,

$$F^{(\text{corr})} \longrightarrow -F^{(0+1)} \quad (150)$$

The behavior of $F^{(0+1)}$, $F^{(\text{corr})}$, and their sum $(F^{(0+1)} + F^{(\text{corr})})$ as a function of internuclear distance is illustrated in Fig. 8. This shows that while $F^{(0+1)}$ and $F^{(\text{corr})}$ each approach some non-zero limit as the atoms separate, their sum, $F^{(0+1)} + F^{(\text{corr})}$, correctly goes to zero. The behavior of the components of the relaxation energies, Eqs. (144a)-(144c), as a function of internuclear distance is shown in Fig. 9. Qualitatively these correlated relaxation curves resemble those in Fig. 4 except that it is apparent that they fall off to zero much more quickly than their first-order counterparts in Fig. 4. We note that again the kinetic energy and the electron-nuclear attraction energies yield the largest contributions to the total relaxation energy. The linear relaxation in the electron-electron repulsion energy is shown in Fig. 9 to remain comparatively slowly varying with internuclear distance, the same as was found earlier for its first-order counterpart in Fig. 4. This indicates that this energy contribution has little or no role in determining the equilibrium bond length in this case. The non-linear effect, $\delta^2 E_{ee}^{CI}$, is found to be negligible in comparison and is therefore omitted from Fig. 9.

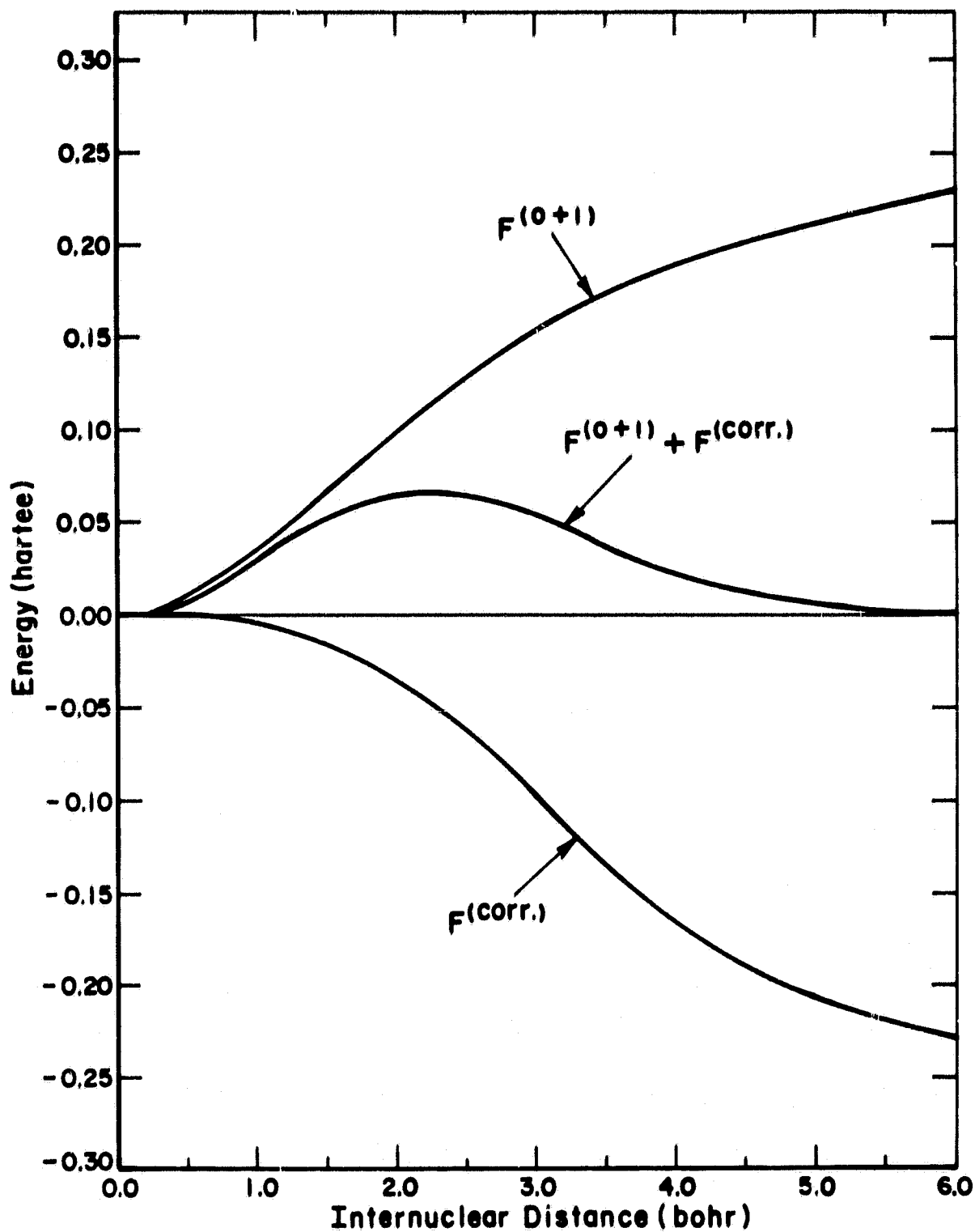


FIG. 8. The term causing the incorrect long-range behavior in the ASED energy through first-order, $F^{(0+1)}$, its counterpart in the correlation energy, $F^{(corr.)}$, and their sum as a function of internuclear distance for the H_2 molecule in the $X^1 \Sigma_g^+$ state.

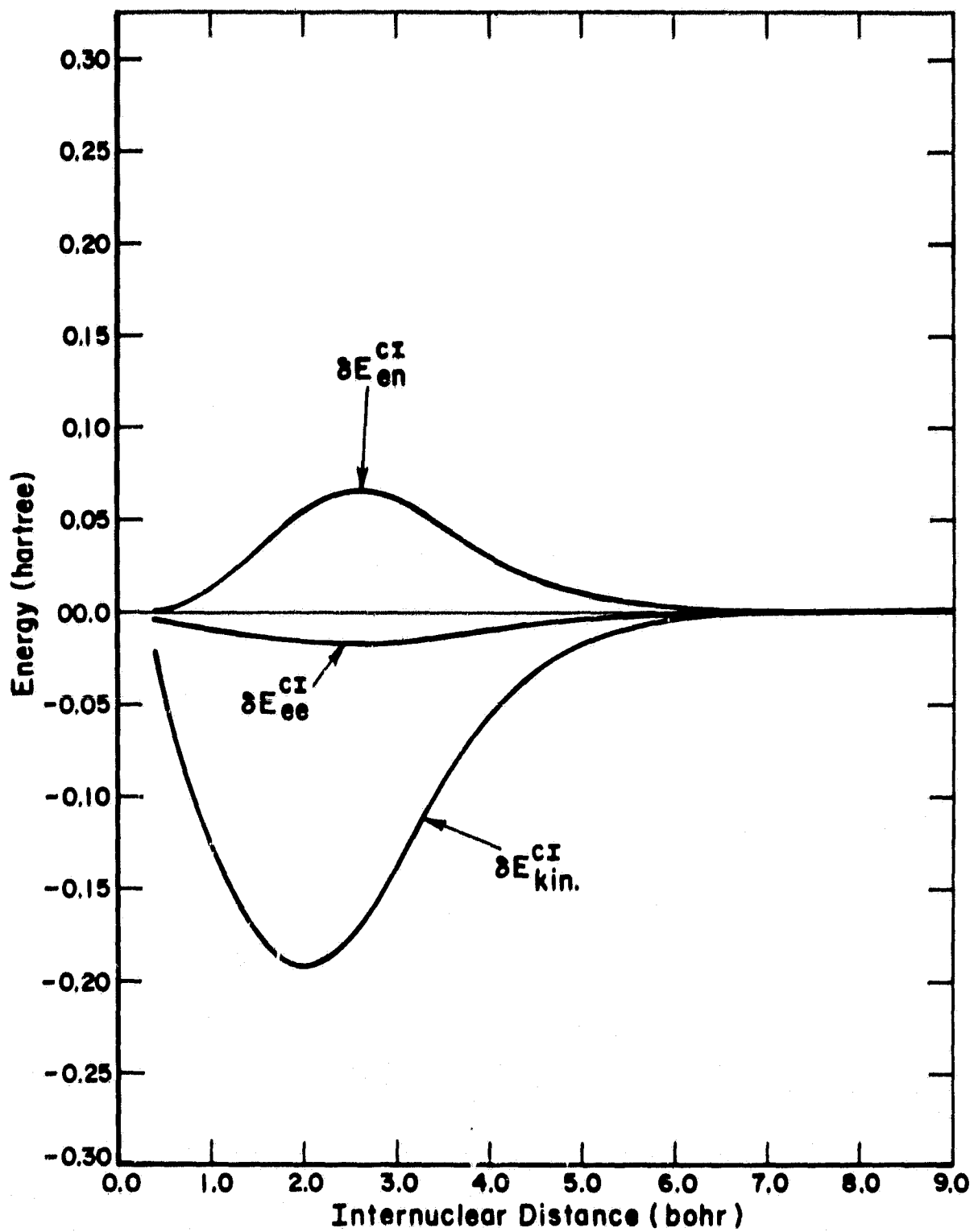


FIG. 9. The relaxation in the various components of the correlated electronic energy as a function of internuclear distance, for the H_2 molecule in the $X^1 \Sigma_g^+$ state.

Figure 10 shows the effects on the ASED potential energy curve of the inclusion of correlation corrections. The two reference potential curves in this figure are the previously obtained (see Fig. 7) partial first-order ASED energy

$$\Delta E_{\text{ASED}}^{(0+1)} - F^{(0+1)} = E_{el} + \delta E_{el}^{(0+1)} \quad (151)$$

and the full CI potential energy curve, ^(47,50) $\Delta E_{\text{CI}}^{2 \times 2}$. The latter represents the best possible result attainable given the present particular choice of basis set. The first-order ASED energy with $F^{(0+1)}$ corrected by $F^{(\text{corr})}$, is shown in Fig. 10 to be a considerable improvement of the potential curve at small internuclear distances up to about the equilibrium distance. At larger internuclear distances, however, the fall-off to zero in this curve is much too slow again, and indeed has a peculiar shape. In contrast, the partial correlated ASED energy (the analog to Eq. (151)),

$$\Delta E_{\text{ASED}}^{\text{CI}} - F^{(0+1)} - F^{(\text{corr})} = E_{el} + \delta E_{el}^{\text{CI}}, \quad (152)$$

exhibits the correct fall-off to zero at larger internuclear distances, but fails to attain good agreement with the full CI curve at smaller internuclear distances. The two correlation effects at play here are the effect at smaller internuclear distances of adding $F^{(\text{corr})}$, and the effect at larger internuclear distances of the improved fall-off rate of the correlated relaxation energies (see Fig. 9). When both these factors are combined one obtains $\Delta E_{\text{ASED}}^{\text{CI}}$. This is shown in Fig. 10 to be in excellent agreement with the full CI potential energy curve. ⁽⁵⁰⁾ The small discrepancies that remain are due to the neglect of effects on

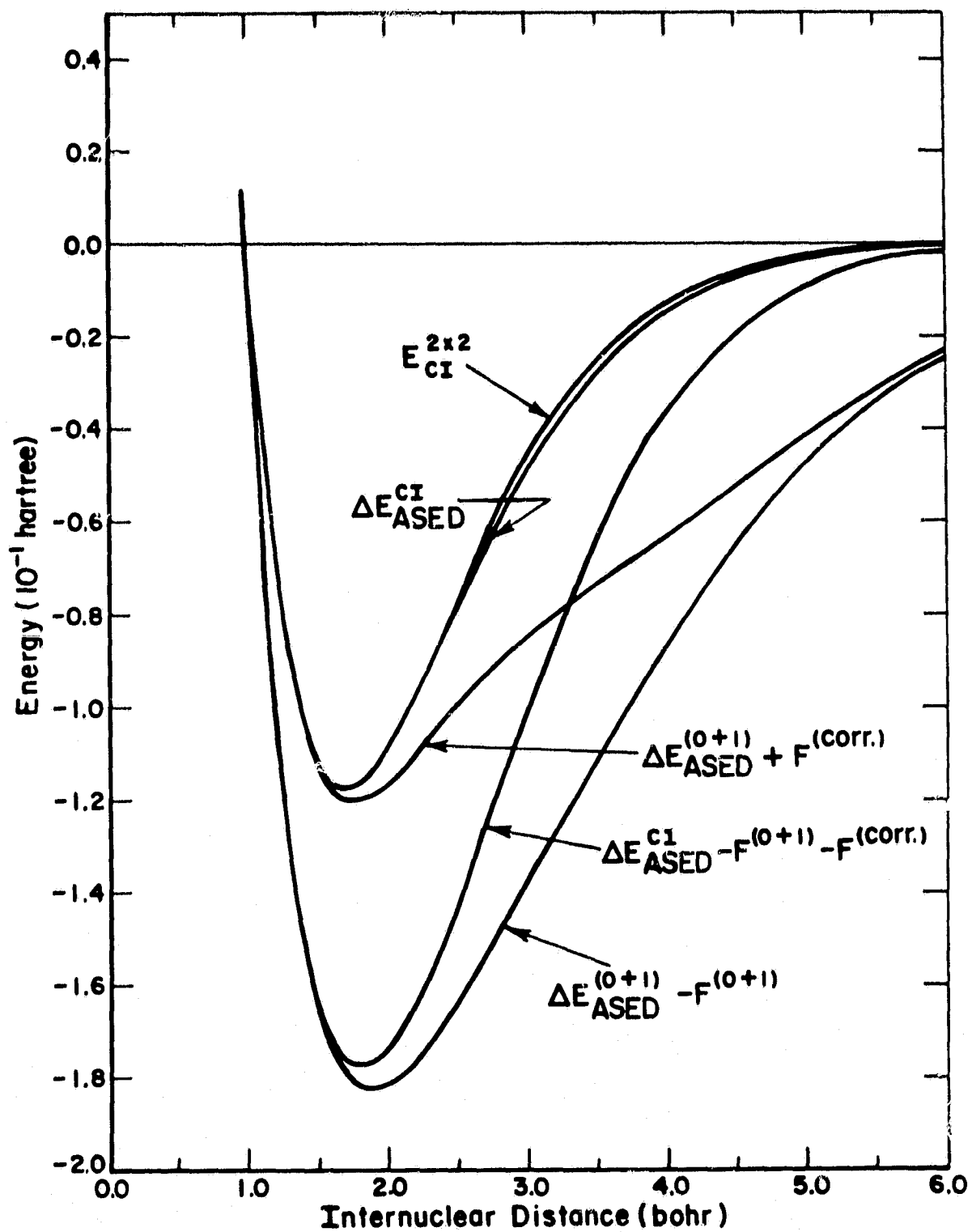


FIG.10. Comparison of ASED potential energy curves resulting from various levels of inclusion of electron correlation effects, and the full CI potential curve⁽⁵⁰⁾, for the H_2 molecule in the $X^1\Sigma_g^+$ state.

the matrix elements that are non-linear in the relaxation of the one-electron density matrix. The energy associated with the non-linear effects is

$$\delta^2 E_{el}^{CI} = \begin{pmatrix} c_1 & c_2 \end{pmatrix} \begin{pmatrix} \delta^2 H_{11} & \delta^2 H_{12} \\ \delta^2 H_{12} & \delta^2 H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \quad (153)$$

where

$$\delta^2 H_{ij} = 1/4 \iint \frac{1}{\|\underline{r} - \underline{r}'\|} \delta_{ij}^{(1)}(\underline{r}) \delta_{ij}^{(1)}(\underline{r}') d\underline{r} d\underline{r}' \quad (154)$$

In addition to the contribution through Eq. (153), the non-linear relaxation effects modify the solutions to the CI secular equation, Eqs. (147) and (148), and through this they also affect the linear relaxation terms E_{el}^{CI} and $F^{(corr)}$. In the present case, however, we find these non-linear relaxation contributions to be negligible.

C. The He₂ Molecule

The LiH and H₂ molecules are examples, respectively, of the most favorable cases and the most complicated cases for the application of the ASED energy decomposition. There exist also cases of intermediate complication in which the ASED first-order energy does approach the separated atoms limit correctly, but for which the exchange energy appears in the least tractable form because the molecular orbitals are symmetry functions. An example illustrating this intermediate case is found in the He₂ molecule in the $X^1\Sigma_g^+$ state. The ASED zero-order wavefunction is

$$\psi^{(0)} = A \left(1\sigma_g^2 1\sigma_u^2 \alpha\beta\alpha\beta \right) \quad (155)$$

where the ASED occupied molecular orbitals approach the limits

$$1\sigma_g \longrightarrow \frac{1}{\sqrt{2}}(1s_A + 1s_B) \quad (156a)$$

$$1\sigma_u \longrightarrow \frac{1}{\sqrt{2}}(1s_A - 1s_B) \quad (156b)$$

as the He atoms separate. The two helium atom orbitals are labeled $1s_A$ and $1s_B$ respectively. The exchange energy in the He_2 molecule case is

$$E_{xch}^{(1)} = -K_{1\sigma_g, 1\sigma_g} - 2K_{1\sigma_g, 1\sigma_u} - K_{1\sigma_u, 1\sigma_u} \quad (157)$$

The linear relaxation of the exchange energy in this form is

$$\delta E_{xch}^{(1)} = - \int_{\mathbf{r}'=\mathbf{r}} \left(\hat{K}_{1\sigma_g^0} + \hat{K}_{1\sigma_u^0} \right) \delta_\rho^{(1)}(\mathbf{r}, \mathbf{r}') d\mathbf{r} \quad (158)$$

where the limit orbitals, Eq. (156), are denoted by $1\sigma_g^0$ and $1\sigma_u^0$.

The exchange operators appearing in Eq. (158) are yet fully molecular-type operators. The practical advantages that derive from being able to express the relaxation energy as the expectation value of atomic-like operators are non-existent in the present form. However, one can reexpress the ASED energy in terms of an equivalent set of orbitals. A convenient equivalent set of orbitals is defined as

$$1\sigma_A = \frac{1}{\sqrt{2}}(1\sigma_g + 1\sigma_u) \quad (159a)$$

$$1\sigma_B = \frac{1}{\sqrt{2}}(1\sigma_g - 1\sigma_u) \quad (159b)$$

These orbitals have the property that, as the atoms separate, they approach the atomic orbitals themselves,

$$1\sigma_A \longrightarrow 1s_A \quad (160a)$$

$$1\sigma_B \longrightarrow 1s_B \quad (160b)$$

The exchange energy in terms of these orbitals is

$$E_{\text{exch}}^{(1)} = -K_{1\sigma_A, 1\sigma_A} - 2K_{1\sigma_A, 1\sigma_B} - K_{1\sigma_B, 1\sigma_B} \quad (161)$$

and the linear relaxation in the exchange energy is

$$\delta E_{\text{exch}}^{(1)} = \int_{\underline{r}' = \underline{r}} \left(-\hat{K}_{1s_A} - \hat{K}_{1s_B} \right) \delta_{\rho}^{(1)}(\underline{r}, \underline{r}') \, d\underline{r} \quad (162)$$

We note that, by the choice of this equivalent set of orbitals in terms of which to construct the exchange energy, one can once again express the linear relaxation in the exchange energy as the expectation value of atomic-like exchange operators. The relaxation in the one-electron density matrix in this case is

$$\delta_{\rho}^{(1)}(\underline{r}, \underline{r}') = \rho^{(1)}(\underline{r}, \underline{r}') - \rho^{\text{sup}}(\underline{r}, \underline{r}') \quad (163a)$$

where

$$\rho^{(1)}(\underline{r}, \underline{r}') = 2(1\sigma_A \cdot 1\sigma_A) + 2(1\sigma_B \cdot 1\sigma_B) \quad (163b)$$

and

$$\rho^{\text{sup}}(\underline{r}, \underline{r}') = 2(1s_A \cdot 1s_A) + 2(1s_B \cdot 1s_B) \quad (163c)$$

The total linear relaxation energy is again the expectation value of a Fock operator

$$\delta E_{\text{ASED}}^{(0+1)} = \int_{\underline{r}'=\underline{r}} \hat{F}_{\delta\rho}^{(1)}(\underline{r}, \underline{r}') d\underline{r} \quad (164)$$

where, as a result of the transformation to the equivalent orbitals, the Fock operator contains superpositions of atomic effective potentials,

$$\hat{F} = -1/2 \nabla^2 + \left[-\frac{2}{r_A} + (2\hat{J}_{1s_A} - \hat{K}_{1s_A}) \right] + \left[-\frac{2}{r_B} + (2\hat{J}_{1s_B} - \hat{K}_{1s_B}) \right] \quad (165)$$

D. General properties

We conclude with some observations about the general properties of the ASEd energy decomposition. The calculation of the ASEd molecular orbitals, Eqs. (48)-(58), appears to require only the evaluation of one-electron type of integrals, while avoiding the calculation of the numerous two-electron multi-center type of integrals. The calculation

of the ASED molecular energy through first-order, Eq. (91), also appears to offer similar practical advantages over the calculation by the traditional approaches of the molecular energy. The E_{cl} component of the ASED energy is a pair-wise additive term. Each pair contribution requires at most the calculation of two-center two-electron integrals. The techniques dealing with this particular type of calculation have been extensively developed and refined.⁽⁵¹⁻⁵⁶⁾ Moreover, these two-center energies in E_{cl} can be calculated prior to their use in a polyatomic molecule calculation. In many cases, the same practical advantages exist in the calculation of $E_{xch}^{(1)}$ by partitioning it into E_{xch}^0 and the relaxation terms $\delta E_{xch}^{(1)}$ and $\delta^2 E_{xch}^{(1)}$. This advantage may only exist, however, after reexpressing $E_{xch}^{(1)}$ in an equivalent set of orbitals. The linear relaxation energies, Eqs. (92) and (93), are just expectation values of Fock-operators containing superpositions of short-ranged atomic-like potentials. This lends itself to the use of matrix-representations of these atomic-like potentials in an atomic basis set, in a manner analogous to the procedures discussed in solving for the molecular orbitals. The practical problem of evaluating the linear relaxation energy thus reduces to the calculation of the projection of the relaxation in the one-electron density-matrices onto the various atomic orbital spaces. Provided the non-linear relaxation effects remain minor, the calculation of the molecular energy via the ASED approach has the prospect of avoiding the most time-consuming practical aspects of the traditional approaches. Complications, however, remain yet to be fully resolved in those cases when a limited CI is required because the ASED energy, through first-order, does not approach the separated-atoms limit correctly. On the other hand, it is apparent

that each of the CI hamiltonian matrix elements may themselves be decomposed as we have done for the zero and first order ASED energies. The latter are in fact just a prototype of a diagonal hamiltonian matrix element. Such a decomposition of the CI matrix-elements, aided possibly by first formulating these elements in terms of equivalent orbitals, has prospects of resolving the problem with the correct long-range behavior of the ASED energy. Moreover, such an ASED decomposition of the CI hamiltonian matrix has some interesting simplifying aspects in its own right for use in CI calculations. The tailoring of the molecular orbitals to lead to a convenient decomposition of the total molecular energy is well known from its use in the PCILO method.^(57,58) The use of the properties of the solutions to the atomic and diatomic subproblems for simplifying the calculation of the polyatomic molecular energy as in the present ASED method is also commonly used in the well known approach of atoms-and-diatomics-in-molecules.⁽⁵⁹⁻⁶¹⁾ Finally, we note that the ASED energy decomposition may be applied without further change to just the valence electrons by using, for example, the method of effective core potentials⁽⁶²⁾ to remove the core electrons from explicit consideration. Relativistic effects on the valence electrons may also be incorporated into the ASED energy decomposition without further change via the effective core potentials.⁽⁶²⁾

V. CONCLUSION

We have presented a decomposition of the molecular energy. This particular decomposition is motivated by Anderson's ASED model of chemical bonding.^(5,26) The energy through first-order is found to adopt the form of the classical electrostatic energy, of a zero-order exchange energy, and of various relaxation energies. The latter give the effect on the energy of the relaxation in the one-electron density-matrix relative to the superposition of atomic one-electron density-matrices. We have illustrated three different possible cases using the $\text{LiH } X^1\Sigma^+$, $\text{H}_2 X^1\Sigma_g^+$, and $\text{He}_2 X^1\Sigma_g^+$ molecules as examples. The ASED approach presented here has the advantage of dividing the energy into physically transparent group of terms. Moreover, the form of the terms in the ASED energy lends itself to the fullest utilization of properties of the atomic solution in order to simplify the calculation of the molecular energy. The result is that at most two-center two-electron type of integrals are needed for a calculation if non-linear relaxation effects remain of minor importance. Thus, the ASED approach presented here has prospects of reducing even by an order of magnitude the effort required in the calculation of the molecular energy by the conventional approaches.^(1,2)

VI. ACKNOWLEDGEMENTS

Support of this work by NASA-Ames Research Center under Grant NSG-2027 is gratefully acknowledged. We wish to thank Dr. Alfred Anderson for stimulating conversations about his work on the ASED approach, and Dr. David Cox and Dr. Frank Bobrowicz for helpful discussions on some aspects of this work.

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FIGURE CAPTIONS

- FIG. 1. The electrostatic energy E_R , the exchange energy $H_{A,B}$, and the total energy change ΔE as a function of internuclear distance for the H_2^+ molecule in the $X^2\Sigma_g^+$ state.
- FIG. 2. Comparison of various ASED potential energy curves for the H_2^+ molecule in the $X^2\Sigma_g^+$ state with the minimum basis set variational energy⁽¹⁵⁾ and the exact potential energy curve.⁽²⁴⁾
- FIG. 3. The zero-order electronic energy $\Delta E_{el}^{(0)}$, the classical electrostatic energy E_{cl} , and the net ASED zero-order potential energy, $\Delta E_{ASED}^{(0)}$, as a function of internuclear distance for the H_2 molecule in the $X^1\Sigma_g^+$ state. The exact potential energy curve⁽⁴⁶⁾ is also shown for purposes of comparison.
- FIG. 4. The relaxation in the various components of the electronic energy as a function of internuclear distance, for the H_2 molecule in the $X^1\Sigma_g^+$ state.
- FIG. 5. Decomposition of the partial ASED energy through first-order, $\Delta E_{ASED}^{(0+1)} - F^{(0+1)}$, into the classical electrostatic energy, E_{cl} , and the relaxation energy, $\delta E_{cl}^{(0+1)}$, for the H_2 molecule in the $X^1\Sigma_g^+$ state.
- FIG. 6. Decomposition of the partial ASED energy through first-order, $\Delta E_{ASED}^{(0+1)} - F^{(0+1)}$, into an effective electrostatic energy, $E_{cl} + \delta E_{en}^{(0+1)} + \delta E_{ee}^{(0+1)}$, and the relaxation in the kinetic energy, $\delta E_{kin}^{(0+1)}$, for the H_2 molecule in the $X^1\Sigma_g^+$ state.

FIGURE CAPTIONS
(Continued)

- FIG. 7. Comparison of the partial ASED energy through first-order, $\Delta E_{\text{ASED}}^{(0+1)} - F^{(0+1)}$, with the Hartree-Fock⁽⁴⁷⁾ and the exact⁽⁴⁶⁾ potential energy curves, for the H_2 molecule in the $X^1 \Sigma_g^+$ state.
- FIG. 8. The term causing the incorrect long-range behavior in the ASED energy through first-order, $F^{(0+1)}$, its counterpart in the correlation energy, $F^{(\text{corr})}$, and their sum as a function of internuclear distance for the H_2 molecule in the $X^1 \Sigma_g^+$ state.
- FIG. 9. The relaxation in the various components of the correlated electronic energy as a function of internuclear distance, for the H_2 molecule in the $X^1 \Sigma_g^+$ state.
- FIG. 10. Comparison of ASED potential energy curves resulting from various levels of inclusion of electron correlation effects, and the full CI potential curve⁽⁵⁰⁾, for the H_2 molecule in the $X^1 \Sigma_g^+$ state.