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EFFECTIVE HAMILTONIAN METHOD FOR ENVIRONMENTAL EFFECTS

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Abstract

Some novel physical ideas and mathematical techniques are described, useful in the development of effective Hamiltonian methods for studying molecular environmental effects.

1. Introduction

There are a number of physical and chemical phenomena that are expected to be understood in terms of localized electronic states. Defects and impurities in a crystal, chemisorbed atoms and molecules, and transition metal ions embedded in a crystalline surrounding are some of the examples. Also, there is a traditional notion that many characteristics of constituent parts of a large molecule, such as bond lengths, bond angles, spectroscopic force constants, etc., are more or less local entities.

Theoretically, however, the localized electronic state is not well defined because of the intrinsic ambiguity in spatial form of individual one-electron functions with which the total wave function of the system is constructed. Dichotomy of the MO theory and the VB theory is just one manifestation of the ambiguity.

In the present work, the problem of localizability of electronic states is approached from a pragmatic point of view. The approach is based on a finite cluster model. It consists of two parts: (I) the theatre for localized electronic phenomena, and (II) the surrounding environment (see fig. 1). Atoms in region (I) contribute all or part of their electrons to the theatre, while electrons in region (II) remain basically dormant.

We initiate a proving calculation with a rather small size of region (I) and with region (II) of an appropriate size large enough to avoid any artificial frontier

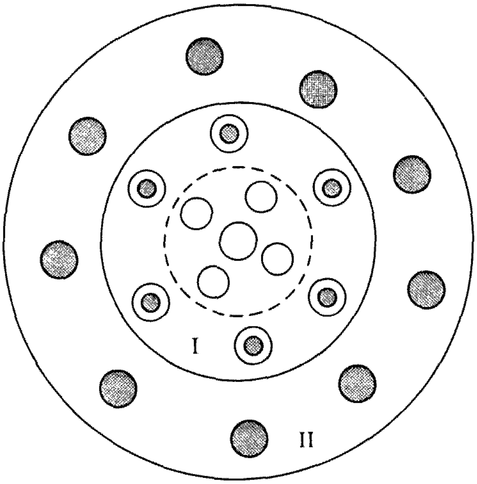

Fig. 1. Cluster structure.

effect. We then increase the size (the number of atoms involved) of region (I) with region (II) adjusted accordingly. If the computed electronic properties of the system become stabilized and insensitive to the change of size of the cluster, we take it as the indication of establishment of the localized electronic state.

In order to carry out the computational procedure in a reliable way to the converging conclusion, it is imperative to develop an efficient ab initio calculational algorithm that enables us to treat a system of a fairly large number of atoms with theoretical confidence. It will defeat our original purpose of establishing the localizability computationally if we are forced to stop before reaching the state of convergence.

In the following sections, some useful physical ideas and mathematical techniques are described to develop an efficient ab initio computational scheme to handle the system schematically shown in fig. 1. It contains three types of circular figures, unshaded circles, partially shaded and fully shaded ones. In the simplest and common situation they represent atoms with different degrees of freezing the electron orbital functions. How to represent these atoms à la ab initio, that is, without using parameters to be adjusted according to some experimentally obtained quantities, is the central theme of the following theoretical discussions. It is to be noted that those circular figures in fig. 1 can themselves be certain molecular entities such as various ligands in metal complexes or functional groups identified as such in large molecules. The mathematical techniques described in the following are flexible enough to deal with them.

The theoretical development in the present paper is an extension of the formalism proposed and successfully applied by Barandiarán and Seijo [1,2], where much relevant literature is cited.

2. Mathematical techniques

2.1. SPECTRAL REPRESENTATION OF OPERATORS

The spectral representation of a linear operator is a powerful mathematical notion. Here, we pick up a portion of the concept as a convenient mathematical technique tailored for our purpose.

Let O be a one-electron operator and ϕ and ψ be two one-electron orbital functions, and let us consider the integral (matrix element),

$$I = \langle \phi \mid O \mid \psi \rangle. \tag{2.1}$$

If we expand ϕ and ψ by a complete set of orthonormal basis functions $\{f_i\}$,

$$\langle \phi | = \sum_i \langle \phi | f_i \rangle \langle f_i |,$$

$$| \psi \rangle = \sum_j | f_j \rangle \langle f_j | \psi \rangle, \tag{2.2}$$

then we have

$$I = \sum_i \sum_j \langle \phi | f_i \rangle \langle f_i | O | f_j \rangle \langle f_j | \psi \rangle = \langle \phi | P O P | \psi \rangle, \tag{2.3}$$

where

$$P = \sum_i | f_i \rangle \langle f_i | \tag{2.4}$$

is a projection operator, $P^2 = P$. Comparing (2.1) and (2.3), we identify

$$P O P = \sum_i \sum_j | f_i \rangle \langle f_i | O | f_j \rangle \langle f_j | \tag{2.5}$$

as a spectral representation of an operator O.

If POP has some computational advantage over the original operator O, the representation, a "coating" of an operator with a basis function set $\{f_i\}$, becomes a useful computational tool, as shown in the development of the effective Hamiltonian method for molecules [3].

In practice a finite, n-membered, non-orthogonal basis function set $\{\chi_p\}$ is used with a real symmetric overlap matrix:

$$\{\chi_p\}, \quad p = 1, 2, \ldots, n,$$

$$S_{pq} = \langle \chi_p | \chi_q \rangle = S_{qp}. \tag{2.6}$$

This is a commonly encountered situation in the Roothaan–Hall finite expansion method. In terms of $\{\chi_p\}$,

$$P=\sum_{p}\sum_{q}|\chi_p\rangle(\mathrm{S}^{-1})_{pq}\langle\chi_q| \tag{2.7}$$

and

$$\begin{aligned}POP&=\sum_{pq}\sum_{rs}|\chi_p\rangle(\mathrm{S}^{-1})_{pq}\langle\chi_q|O|\chi_r\rangle(\mathrm{S}^{-1})_{rs}\langle\chi_s| \\ &=\sum_{pq}|\chi_p\rangle(\mathrm{S}^{-1}\mathrm{O}\mathrm{S}^{-1})_{pq}\langle\chi_q|.\end{aligned} \tag{2.8}$$

Since the basis set $\{\chi_p\}$ is not complete, the representation POP in (2.8) is no longer equivalent to the original operator O, but can still be an acceptable approximation to the original. For example, if the effect of the operator O is limited spatially within a short range and the electron orbital functions ϕ and ψ themselves are also in the linear combination of $\{\chi_p\}$, POP can be a good replacement of O in the calculation of the integral I of (2.1).

2.2. ENERGY SHIFT OPERATORS

The total Hamiltonian for N electrons in an atom is written in atomic units as

$$\begin{aligned}&H(1,2,\ldots,N)=\sum_{i}^{N}h(i)+\sum_{i>j}^{N}(1/r_{ij}),\\ &h(i)=-(\Delta_i/2)-(Z/r_i).\end{aligned} \tag{2.9}$$

A unified Fock operator for the determination of Hartree–Fock one-electron orbitals $\{\phi_i\}$ can be derived from H as

$$\begin{aligned}&F|\phi_i\rangle=\varepsilon_i|\phi_i\rangle,\\ &F=-(\Delta/2)-(Z/r)+\sum_{i}(\alpha_i J_i-\beta_i K_i)+R,\end{aligned} \tag{2.10}$$

where R is an operator to ensure proper handling of open-shell electron configurations but not our concern at this moment.

Suppose the Hartree–Fock equation has been solved and the solution orbitals $\{\phi_i\}$ have been obtained. F is expressed in terms of the orbitals $\{\phi_i\}$ and it is a one-electron operator. By adding to F a group of energy shift operators

$$\begin{aligned}&\sigma=\sum_{k}d_k|\phi_k\rangle\langle\phi_k|,\\ &F\to F+\sigma,\end{aligned} \tag{2.11}$$

we may rearrange the energy eigenvalue spectrum of the original Hartree–Fock eq. (2.10) without disturbing the shape of the eigenfunctions:

$$\left[F + \sum_k d_k |\phi_k\rangle\langle\phi_k|\right]|\phi_i\rangle = (\varepsilon_i + d_i)|\phi_i\rangle. \tag{2.12}$$

The value of d_i can be chosen according to the need of shifting the position of the energy eigenvalue of ϕ_i to a certain position in the spectrum. This mathematical technique has been used extensively in the model potential method to establish the effective Hamiltonian and the Fock operator for valence electrons in atoms and molecules. However, the use has not to be limited to the core–valence division. Choice of positive values of $\{d_i\}$ can cover even all occupied orbitals $\{\phi_i\}$. Then the operator $F + \sigma$ represents a group of dormant (frozen) electrons but electron waves from outside can still penetrate into the frozen atomic entity by the wave components orthogonal to the occupied orbitals (see fig. 2(a)). This idea of varied degree of freezing could be useful for the treatment of the environmental region of our cluster model (fig. 1).

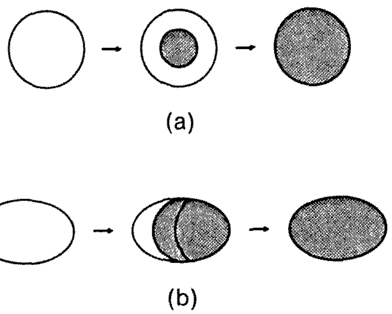

Fig. 2. Changing frozen area in atoms and molecules. In (b), the frozen area may not be surrounded by the active area.

3. Formalism for atoms and molecules

3.1. ATOMS

Various forms of the effective Hamiltonian for valence electrons in an atom have been proposed and used to economize molecular calculation of molecular systems containing heavy atoms. Many of them are claimed to be of an ab initio method in the sense that the method is free of parameters determined by using experimental data. Among these ab initio methods, the ab initio model potential (AIMP) method developed mainly by Seijo and Barandiarán [4] occupies a unique position. In the AIMP method, the core model potentials are constructed from the sole knowledge of frozen core orbitals *without* using valence orbitals and valence orbital energies of the reference all-electron atomic calculation.

The total Hamiltonian for N *valence* electrons of an atom in the frozen core approximation may be written in atomic units as

$$H(1,2,\ldots,N)=\sum_{i}^{N}h(i)+\sum_{i>j}^{N}(1/r_{ij}),$$

$$h(i)=-(\Delta_i/2)-(Z-Z_{\text{core}})/r_i+V_{\text{core}}(i)+\sigma(i), \tag{3.1}$$

where

$$V_{\text{core}}=-Z_{\text{core}}/r_i+\sum_{c}^{\text{core}}[2J_c(i)-K_c(i)],$$

$$\sigma(i)=-\sum_{c}^{\text{core}}2\varepsilon_c|\phi_c\rangle\langle\phi_c|. \tag{3.2}$$

Z_{core} is the number of core electrons times the unit charge e. The operator V_{core} represents the effect of the frozen core electrons on the valence electrons and the shift operator σ enforces the core–valence orthogonality, preventing the valence orbitals from collapsing onto the core space.

In the AIMP method, V_{core} is divided into two parts,

$$V_{\text{core}}(i)=V_{\text{coul}}(i)+V_{\text{exch}}(i), \tag{3.3}$$

where

$$V_{\text{coul}}(i)=-Z_{\text{core}}/r_i+2\sum_{c}^{\text{core}}J_c(i),$$

$$V_{\text{exch}}(i)=-\sum_{c}^{\text{core}}K_c(i),$$

and only the non-local exchange operator $V_{\text{exch}}(i)$ is subjected to the spectral representation discussed before. The first part $V_{\text{coul}}(i)$ is actually a local spherical potential and can be expressed in any desired degree of accuracy in the following analytical form [4]:

$$V_{\text{coul}}(i)\equiv V_{\text{coul}}(r_i)$$

$$\cong V_{\text{coul,MP}}(r_i)=\sum_{k}A_k\exp(-\alpha_k r_i^2)/r_i, \tag{3.4}$$

where the parameters $\{A_k,\ \alpha_k\}$ are determined through least-squares fitting to $V_{\text{coul}}(r_i)$, which is completely determined in terms of the core orbitals obtained in the reference all-electron atomic calculation. Therefore, the parameters $\{A_k,\ \alpha_k\}$ are responsible for the accuracy of the fitting but they are not adjustable parameters in the method.

It is, however, possible to eliminate these fitting parameters altogether by applying the technique of spectral respresentation to the entire $V_{\mathrm{core}}(i)$ operator in (3.3):

$$V_{\mathrm{core}}(i) \rightarrow P(i)V_{\mathrm{core}}(i)P(i) \equiv U_{\mathrm{core}}(i),$$

$$P(i) = \sum_{p}\sum_{q} |\chi_p(i)\rangle (\mathrm{S}^{-1})_{pq} \langle \chi_q(i)|. \tag{3.5}$$

A natural choice of the representation basis set $\{\chi_p\}$ in the projection operator $P(i)$ is a set of primitive functions obtained by decontracting contracted basis functions used in the reference all-electron atomic calculations. This choice of representation basis has given satisfactory numerical results in a test calculation [5]. If there is any indication of lack of accuracy, the representation basis can be supplemented at both ends of large and small orbital exponents.

3.2. MOLECULES

The Hamiltonian for N valence electrons of a molecule may be written as

$$H(1,2,\ldots,N) = \sum_{i} h(i) + \sum_{i>j} (1/r_{ij}) + \sum_{I>J} V_{IJ}(R_{IJ}),$$

$$h(i) = -(\Delta_i/2) - \sum_{I} (Z^I - Z^I_{\mathrm{core}})/r_I + \sum_{I} U^I_{\mathrm{core}}(i) + \sum_{I} \sigma^I(i),$$

$$V_{IJ}(R_{IJ}) = (Z^I - Z^I_{\mathrm{core}})(Z^J - Z^J_{\mathrm{core}})/R_{IJ}. \tag{3.6}$$

The core-electron operator $U^I_{\mathrm{core}}(i)$ determined for atom I is carried over to the molecular Hamiltonian without change. V_{IJ} represents the internuclear repulsion between nuclei I and J spherically screened by the core electrons. The above Hamiltonian has been tested for N_2, P_2 and As_2 on the Hartree–Fock level and the result is generally satisfactory [5].

For spherically shaped frozen core regions, the method of Seijo and Barandiarán [4], in which V_{coul} in (3) is explicitly expressed as a local potential, could be more economical than the approach that includes both V_{coul} and V_{exch} in (3.3) in the spectral representation. However, the latter approach offers an attractive possibility of representing *non*-spherical frozen areas (fig. 2(b)). As discussed in some detail elsewhere [3], the spectral representation can be applied to a variety of quantum mechanical operators including Coulomb (J) and exchange (K) operators of arbitrary spatial shape. For example, an effective Hamiltonian may be constructed for two lone-pair electrons of NH_3 as the two active electrons, with the rest as a frozen area of pyramidal shape. A similar idea may also be applied to a planar C_2H_4

with the σ-skeleton as the cores, leaving two π electrons as the active electrons. Furthermore, as indicated toward the end of the previous section, the representation can be applied to an entire molecule as a building block of the outermost environmental region (see fig. 2(b)). It is now possible to examine the validity of the classic ligand field theory by starting with an all-electron treatment of ligand atoms and molecules and then gradually freezing the electron orbitals until the establishment of the electrostatic ligand field, including multipole effects [3] and guarded by the energy shift operator $\{\sigma^I(i)\}$ in (3.6).

The total energy of the system is calculated from the Hamiltonian (3.6). The energy shift operator term $\sum\sigma$ must be included in the calculation, especially in the matrix element computation of the electron correlation calculations in which the entire virtual space is used.

4. Approximate Fock operator for a cluster

In this section, we describe another theoretical idea that may enable us to conduct a quantum mechanical treatment of a large cluster. In our cluster model schematically illustrated in fig. 1, the entire body, the region (I) + the region (II), is regarded as a finite cluster. Atoms and molecules in region (I) contribute electrons to the total wave function of the system, but there is no contribution of electrons from region (II). A more common definition of a cluster would be region (I) only, with region (II) regarded as the environment surrounding the cluster. Barandiarán and Seijo [1] presented an AIMP formalism for such a cluster-environment system and their formulation can be easily generalized to cover the cluster model of the present paper.

As indicated by the partiallly shaded circles in fig. 1, the inner cluster region (I) has the "gray" area. Atoms and molecules there do contribute electrons to the total wave function but with varied degree. As explained in the introduction, one of the primary objectives of the present work is to establish a computational mechanism to validate the cluster model, and it is important to develop an approximation to make it feasible to handle a fairly large number of atoms of the gray area in order to achieve that objective, in the case that a straightforward application of the AIMP method of Seijo and Barandiarán, or the ab initio effective Hamiltonian method described in the preceding sections, becomes too laborious and expensive.

Historically, the cluster model was adopted because of our incapability of conducting SCF MO calculations on a large system, and the size of the cluster was dictated critically by the computational feasibility. If we can perform a standard SCF calculation on a large molecular system routinely, the whole outlook of the cluster approximation will change.

The technical trouble associated with an SCF calculation on a system of a large number of atoms possibly containing some transition metal atoms is the convergence (divergence) of the SCF process. The Fock operator is a precisely definable one-electron operator, but the Hartree–Fock equation has to be solved iteratively. On the other hand, the one-electron Hückel Hamiltonian cannot be written down explicitly, but the solution of the Hückel equation is obtained by a non-iterative diagonalization procedure and there is no problem of divergence.

We shall present a one-electron Hamiltonian usable for a large molecule, an approximation to the molecular Fock operator, which can be written down explicitly just as the Fock operator and used as conveniently as the Hückel Hamiltonian. It contains some adjustable parameters, but they are calibrated through atomic and molecular reference calculations. Molecular orbitals and orbital energies are obtained as the eigenfunctions and the eigenvalues of the one-electron operator by non-iterative diagonalization just as in the Hückel method. The method might be nicknamed the ab initio Hückel (abiHück) method. A similar idea was proposed and developed some years ago by Nicolas and Durand [6]. The present work is a variation of their idea.

Many molecules have a closed-shell electron configuration and we shall discuss the closed-shell case, although the method to be developed here is applicable to the open-shell case as well. The total wave function is

$$\Psi = A_{\mathrm{SL}}[\varphi_1(1)\alpha(1)\varphi_1(2)\beta(2)\ \ldots\ \varphi_n(2n-1)\alpha(2n-1)\varphi_n(2n)\beta(2n)], \tag{4.1}$$

and the total energy is

$$\begin{aligned} E &= 2\sum_i^n H_i + \sum_i^n \sum_j^n (2J_{ij} - K_{ij}), \\ H_i &= \langle \varphi_i | -(\Delta/2) - \sum_A (Z^A/r_A) | \varphi_i \rangle, \\ J_{ij} &= \langle \varphi_i | J_j | \varphi_i \rangle, \quad K_{ij} = \langle \varphi_i | K_j | \varphi_i \rangle. \end{aligned} \tag{4.2}$$

The Hartree–Fock equation is

$$\begin{aligned} F\varphi_i &= \varepsilon_i \varphi_i, \\ F &= -(\Delta/2) - \sum_A (Z^A/r_A) + \sum_j (2J_j - K_j). \end{aligned} \tag{4.3}$$

The summation index j runs over the occupied *molecular* orbitals $\{\varphi_j\}$ that are usually expanded with a basis function set $\{\chi_r\}$,

$$\varphi_j = \sum_r \chi_r c_{rj}. \tag{4.4}$$

Then the Fock operator F is expressed as

$$F = -(\Delta/2) - \sum_{A}(Z^A/r_A) + \sum_{rs}(2J_{rs} - K_{rs})\sum_{j} c_{rj}^{*}c_{sj} . \tag{4.5}$$

The basis set $\{\chi_r\}$ is usually a set of functions placed on atomic sites in the molecule,

$$\underbrace{\underbrace{\{\chi_1, \chi_2, \ldots, \chi_t,}_{\text{atom } A \text{ basis}}\ \underbrace{\chi_{t+1}, \ldots,}_{\text{addition}}}_{\text{on site A}}\ \underbrace{\underbrace{\ldots,}_{\text{atom } B \text{ basis}}\ \underbrace{\ldots,}_{\text{addition}}}_{\text{on site B}}\ \underbrace{\underbrace{\ldots}_{}\ldots}_{}\ldots\} \tag{4.6}$$

and each atomic basis function group consists of the atomic basis functions used in the calculation of isolated atom and some additional diffuse and polarizarion functions. The Hartree–Fock–Roothaan equation is

$$\begin{gathered} \mathbf{F}\mathbf{c}_i = \varepsilon_i \mathbf{S}\mathbf{c}_i \\ F_{pq} = \langle \chi_p | F | \chi_q \rangle, \quad S_{pq} = \langle \chi_p | \chi_q \rangle, \end{gathered} \tag{4.7}$$

where F is given in (4.5) and in the fully expanded form,

$$\begin{aligned} F_{pq} &= H_{pq} + \sum_{rs} \mathcal{P}_{pq,rs} D_{rs} , \\ H_{pq} &= \langle \chi_p | -(\Delta/2) - \sum_{A}(Z^A/r_A) | \chi_q \rangle , \\ D_{rs} &= 2\sum_{j} c_{rj}^{*}c_{sj} , \\ \mathcal{P}_{pq,rs} &= [\chi_p\chi_q | \chi_r\chi_s] - \tfrac{1}{2}[\chi_p\chi_s | \chi_r\chi_q] , \\ [ab|cd] &= \iint a^{*}(1)b(1)(1/r_{12})c^{*}(2)d(2)\mathrm{d}v_1\mathrm{d}v_2 . \end{aligned} \tag{4.8}$$

In the semi-empirical all-valence electron SCF method (CNDO, etc.), many different schemes were proposed to obtain approximate values of the matrix elements $\{F_{pq}\}$. Since honest computation of molecular integrals in $\mathcal{P}_{pq,rs}$ is difficult and expensive, various drastic approximations were introduced to simplify the evaluation of the molecular integrals. The ZDO (zero differential overlap) approximation is one of those approximations. This sort of approach may be characterized as microscopic in the sense that individual one-electron and two-electron integrals in F_{pq} were doctored according to the individual types.

In contrast, our approach may be called macroscopic or global because the operator F itself, not individual terms of the matrix element F_{pq}, is treated by an approximation method which might be termed the LCAOP (linear combination of atomic operators) method. Our physical intuition tells us that the effect of the second and third term of the Fock operator (4.5) on electrons may be approximated by the sum of appropriate potential fields assigned to individual atomic sites:

$$\begin{aligned} F &\cong -(\Delta/2) + G_A + G_B + G_C + \ldots \\ &= -(\Delta/2) + \sum_A G_A. \end{aligned} \tag{4.9}$$

There are many possibilities in the choice of the actual form of G_A. In fact, it is theoretically possible to define $\{G_A\}$ such that the equal sign holds in (4.9).

A natural way of molding G_A would be to first establish an atomic Fock operator F_A based on an SCF calculation and then obtain G_A as

$$G_A = F_A + (\Delta/2). \tag{4.10}$$

As commented on the F operator in (2.10), there is a complication in the restricted Hartree–Fock formalism for the open-shell electron configuration, a norm for ground-state atoms. It is possible, however, to prepare a single Fock operator for all the orbitals (closed-shell and open-shell) in the form

$$F_A = -(\Delta/2) - (Z^A/r_A) + \sum_l (a_l J_l - b_l K_l), \tag{4.11}$$

with very slight deviations from the authentic SCF orbitals and orbital energies, if parameters $\{a_l, b_l\}$ are judiciously chosen. Suppose that the SCF calculation for the ground state of atom A is conducted by using the properly parametrized F_A and the expansion basis function set marked "atom A basis" in (4.6). Explicitly,

$$F_A = -(\Delta/2) - (Z^A/r_A) + \sum_{rs\in A} \sum_l (a_l J_{rs} - b_l K_{rs}) c_{rl}^{A^*} c_{sl}^A, \tag{4.12}$$

where

$$\begin{aligned} J_{rs} f(\mathbf{r}) &= \int [\chi_r^*(\mathbf{r}')\chi_s(\mathbf{r}')\,\mathrm{d}\,v'/|\mathbf{r}-\mathbf{r}'|]\, f(\mathbf{r}), \\ K_{rs} f(\mathbf{r}) &= \int [\chi_r^*(\mathbf{r}') f(\mathbf{r}')\,\mathrm{d}\,v'/|\mathbf{r}-\mathbf{r}'|]\,\chi_s(\mathbf{r}), \end{aligned} \tag{4.13}$$

and then from (4.10),

$$G_A = -(Z^A/r_A) + \sum_{rs\in A} \sum_l (a_l J_{rs} - b_l K_{rs}) c_{rl}^{A^*} c_{sl}^A, \tag{4.14}$$

and from (4.9),

$$F_{pq} \equiv \langle \chi_p | -(\Delta/2) | \chi_q \rangle + \sum_A \langle \chi_p | G_A | \chi_q \rangle,$$

$$\langle \chi_p | G_A | \chi_q \rangle = \langle \chi_p | -(\Delta/2) | \chi_q \rangle + \sum_{rs \in A} [\chi_p \chi_q | \chi_r \chi_s] \sum_l a_l c_{rl}^{A*} c_{sl}^{A}$$

$$- \sum_{rs \in A} [\chi_p \chi_s | \chi_r \chi_q] \sum_l b_l c_{rl}^{A*} c_{sl}^{A}. \tag{4.15}$$

Note here that the basis function indices (p, q) cover all the basis functions in (4.6) and therefore in order to compute $\{F_{pq}\}$ from (4.15), we need a majority of molecular integrals over the molecular basis set $\{\chi_p\}$. However, these integrals are to be calculated anyway before the SCF stage of the molecular calculation; $\{F_{pq}\}$ obtained from (4.15) may serve as a good starting point to initiate the SCF process. This is a useful by-product in the application of the LCAOP approximation to the molecular Fock operator.

Now we proceed to treat the operator G_A by an appropriate spectral representation

$$G_A \to P_A G_A P_A,$$

$$P_A = \sum_{kl} | f_k^A \rangle (\mathrm{S}^{-1})_{kl} \langle f_l^A |. \tag{4.16}$$

Then,

$$F_{pq} \sim \langle \chi_p | -(\Delta/2) | \chi_q \rangle + \sum_A \langle \chi_p | P_A G_A P_A | \chi_q \rangle. \tag{4.17}$$

The second term in the above now requires only overlap integrals, thus avoiding costly molecular integral calculation in (4.15). This sort of projection for approximating multicenter integrals was used by Ruedenberg [7] and utilized extensively by Mayer [8]. It can be hoped that this method of computing approximate values of $\{F_{pq}\}$ would enable us to obtain molecular orbitals of good quality over a large cluster system.

The present method involves two steps of approximation. The first is to approximate a genuine molecular Fock operator in the form of a linear combination of atomic operators (LCAOP), and the second is to replace the atomic operators with their spectral representations.

5. Test calculations

The theoretical ideas presented in the preceding section are in the process of preliminary testing. So far, a few test calculations have been done on small molecules. We shall limit ourselves to a cursory review of some preliminary results of the test.

The idea of using formula (4.15) to prepare a starting set of $\{F_{pq}\}$ for the standard SCF molecular calculations was tested for Li_2 and F_2 by using a GAMESS program. Saving has been only in the first three or four SCF iterations in these cases, but the method will prove more useful for more difficult cases.

The abiHück method has been tested for H_2, Li_2, N_2, F_2, LiF, CO, H_2O and Li_2O. Results for H_2, Li_2, N_2, and CH_4 turned out to be more or less acceptable. Table 1 gives the essence of the numberical result for N_2 and table 2 for CH_4. We

Table 1

N_2: total energy and orbital energies [(721/61) CGTO basis set].

	Ordinary SCF (GAMESS)	abiHück
R (a.u.)	E_t (a.u.)	E_t (a.u.)
1.5	− 108.1834	− 107.1009
1.75	− 108.7049	− 107.5299
2.0	− 108.8597	− 107.5497
2.25	− 108.8525	− 107.3984
2.5	− 108.7799	− 107.2053
$R = 2.0$ (a.u.)	ε_i (a.u.)	ε_i (a.u.)
$1\sigma_g$	− 15.736	− 15.646
$1\sigma_u$	− 15.732	− 15.636
$2\sigma_g$	− 1.561	− 1.740
$2\sigma_u$	− 0.765	− 0.703
$1\pi_u$	− 0.652	− 0.477
$3\sigma_g$	− 0.627	− 0.424

Table 2

CH_4: total energy and orbital energies [(721/61) CGTO for C, (51) CGTO for H].

	Ordinary SCF (GAMESS)	abiHück
$R/\sqrt{3}$ (a.u.)	E_t (a.u.)	E_t (a.u.)
0.9		− 39.6058
1.0	− 40.0225	− 39.7794
1.1	− 40.1272	− 39.8037
1.2	− 40.1575	− 39.7423
1.3	− 40.1417	− 39.6323
1.4	− 40.0979	− 39.4952
$R/\sqrt{3} = 1.2$ (a.u.)	ε_i (a.u.)	ε_i (a.u.)
$1a_1$	− 11.249	− 11.355
$2a_1$	− 0.953	− 1.040
$1t_2$	− 0.551	− 0.481

have encountered some serious difficulty producing a proper minimum in the total energy as a function of the internuclear distance for LiF and CO. The bond angle of Li_2O came out correctly to be 180°, but this was not exactly a source of joy because we also obtained a linear H_2O.

Adjustable parameters of the method are $\{a_l, b_l\}$ in (4.14) for each atom. These parameters originate from the vector coupling coefficients of individual atoms and if the orbital l accommodates two electrons, then $a_l = 2$ and $b_l = 1$. Therefore, for filled inner orbitals these fixed values were assigned. For outer orbitals, we adjusted one or two of them to reproduce results of the authentic open-shell restricted Hartree–Fock atomic calculation and then brought them to the molecular calculation. We have been learning the need to introduce some sort of iterative procedure to readjust these parameters in the molecular environment, reminiscent of the ω-technique of the Hückel method. As can be seen in the expression of $\langle \chi_p \mid G_A \mid \chi_q \rangle$ in (4.15), the readjustment of a_l and b_l has something to do with the readjustment of local electron densities, which is bound to happen when atoms with different electronegativities are involved.

We hope that a concrete formulation of the present ideas and approaches will be reported in the near future as a useful approximate method for the quantum mechanical treatment of a large cluster.

6. Relativistic effects

Relativistic effects are very important in many physical and chemical systems to which our cluster model is expected to be applied. We have successfully incorporated the mass–velocity and the Darwin term to our effective Hamiltonian formalism [9,10] based on the work of Wood and Boring [11]. Along the same line, the spin–orbit interaction term to be used in the effective Hamiltonian has also been worked in the form [3]:

$$H_{SO} = (\alpha^2/2)\, B(1/r)\, (\mathrm{d}V_{nl}/\mathrm{d}r) s \cdot l.$$

The quantities B and V_{nl} are completely determined from the Cowan–Griffin–Boring atomic calculation. There is no parameter adjustment, theoretically or otherwise.

These three terms in the approximate relativistic Hamiltonian, mass–velocity, Darwin, and spin–orbit interaction, are particularly suitable for the spectral representation because they are all short-range effects. One of us (O.M.) has succeeded in including the two-electron Breit interaction systematically in his Dirac–Fock atomic calculation. The interaction can also be included in our cluster calculation if the need arises.

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