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Variational Determination of Molecular Orbital Energies in Independent Particle Models

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A simple construction formalism of molecular orbitals is presented in the context of partitioning of the electronic Hamiltonian. As a consequence of the formalism, a variational method of determining molecular orbital energies is proposed. The method is illustrated with the numerical example for the helium atom, whose result is reasonably meaningful.

Success of molecular orbital (MO) theory strongly suggests that the electronic Hamiltonian of a molecular system is often well represented by an independent particle model (IPM) Hamiltonian. Although MO's and MO energies are not inherently physical quantities, they are allowed to describe the physics of the system as conceptual tools of definite physical meanings under an IPM Hamiltonian. The IPM Hamiltonian is, however, almost always implicit in MO theory; MO's, their energies, wave functions, and state energies are determined usually through variational procedure. One may be tempted to think that the IPM Hamiltonian is merely a simple sum of the one-particle Hamiltonians determining MO's, but without any justification by the physical meaning of the one-particle Hamiltonian itself, the thought is generally incorrect. It seems natural to regard the IPM Hamiltonian as the best unperturbed Hamiltonian in the perturbation theory for electron correlation.

On the other hand, various perturbation methods aiming to go beyond the Hartree-Fock (HF) method have been developed using the so-called HF Hamiltonian as an unperturbed Hamiltonian.1–5) However, irrelevance of that choice to molecular problems has been revealed in spite of the physically sound nature of the HF wave function as the zeroth order wave function.6–9)

There are many unperturbed Hamiltonians having an identical wave function as an eigenfunction; what is the best unperturbed Hamiltonian? After Epstein's suggestive work on this problem,10) taking the unphysical nature of the virtual HF orbitals into account, Silverstone and Yin have exploited the non-HF unperturbed Hamiltonian, the zeroth order wave function still remaining the HF one.11) Davidson has also investigated some related aspects extensivly.12) From a rather different viewpoint, partitioning the wave function space with projection operators,13) an elaborate choice of the unperturbed Hamiltonian has been achieved for the correlation energy calculation by Kutzelnigg.14,15)

This paper has two purposes: One is to present a simple construction formalism of MO's in the context of partitioning of the electronic Hamiltonian. Another is, as a consequence of the formalism, to propose that MO energies are to be adjusted through certain stability condition related to the perturbation left over. The former can be regarded as giving a prescription to extract some practical possibilities from the "unlimited variability"10) concerning selection of the unperturbed Hamiltonian along Silverstone and Yin's way of thinking.11)

Construction of MO's and Partitioning of the Electronic Hamiltonian

Let us start with the electronic Hamiltonian in the second quantized form as

$$H=\sum_{pq}h_{pq}a_p{}^\dagger a_q+\frac{1}{4}\sum_{pqrs}v_{qs}^{pr}a_p{}^\dagger a_r{}^\dagger a_s a_q, \tag{1}$$

where $a_p^\dagger$ and a_p stand for the creation and annihilation operators for the one-electron quantum state p, respectively. Whether the one-electron quantum states form a complete set or not, we regard that the space to be considered is defined by this Hamiltonian.16) The hermiticity is brought in as requirements on the matrix elements:

$$h_{pq}=h_{qp}^{*} \tag{2}$$

and

$$v_{qs}^{pr}=v_{pr}^{qs}{}^{*}. \tag{3}$$

Further we assume that the electron repulsion matrix elements are antisymmetrized in the sense that

$$v_{qs}^{pr}=v_{sq}^{rp}=-\ v_{sq}^{pr}=-\ v_{qs}^{rp}. \tag{4}$$

When we have a starting set $\{p\}$ of one-electron quantum states other than MO's, say, site states, the first step is to generate MO's through an eigenvalue problem

$$\sum_{q}(h_{pq}+x_{pq})c_{qj}=c_{pj}\varepsilon_j^{(0)}, \tag{5}$$

where $\{x_{pq}\}$ is selected so as to give a topologically appropriate nature to the MO's, namely, to $\{c_{pj}\}$; almost exclusively one imposes hermiticity upon $\{x_{pq}\}$ to obtain orthogonal MO's with real eigenvalues. The crucial point in this MO generation step is to separate the space under consideration into two parts, occupied and unoccupied spaces. Denoting sets of the whole, occupied, and unoccupied orbitals, respectively, by M, M_1, and M_2, we have

$$M=M_1\oplus M_2. \tag{6}$$

Though this expression looks rather trivial, it is just an essence of MO theory. The most typical and plausible choice of $\{x_{pq}\}$ is

$$x_{pq}=\sum_{j\in M_1}v_{qj}^{pj}, \tag{7}$$

which leads us to the canonical HF orbitals. Such a choice makes Eq. 5 a pseud-eigenvalue problem; to work out the problem includes self-consistency procedure in general. Through the MO generation step we arrive at the Hamiltonian in the "MO representation"

$$H = \sum_{j} \varepsilon_j^{(0)} a_j^{(0)\dagger} a_j^{(0)} + \frac{1}{4} \sum_{jklm} v_{km}^{jl(0)} a_j^{(0)\dagger} a_l^{(0)\dagger} a_m^{(0)} a_k^{(0)} - \sum_{jk} x_{jk}^{(0)} a_j^{(0)\dagger} a_k^{(0)} \tag{8}$$

and the Fermi sea state

$$|F> = \prod_{j \in M_1} a_j^{(0)\dagger} |\text{ vacuum } >. \tag{9}$$

We label MO's with the indices $\{j,k,\cdots\}$.

Since any unitary transformation within the occupied or unoccupied orbital manifold keeps the Fermi sea state invariant, we can modify MO's (and MO energies) through the following eigenvalue problems.

$$\sum_{k \in M_{\xi\eta}} (\delta_{jk} \varepsilon_j^{(0)} + y_{jk}^{(0)}) u_{kl}^{(1)} = u_{jl}^{(1)} \varepsilon_l^{(1)} \quad (l \in M_{\xi\eta})(\xi = 1,2;\, \eta = 1,2,\cdots) \tag{10}$$

with

$$M_\xi = M_{\xi 1} \oplus M_{\zeta 2} \oplus \cdots \quad (\xi = 1,2). \tag{11}$$

Note that MO indices $\{j,k,\cdots\}$ here are used for both modified(new) and unmodified(old) orbitals. It should be understood that they do not indicate any concrete one-electron function but label MO's flexibly in each orbital manifold. Representatives of MO modifications include the hole potential,[17,18] the electron-hole potential,[19,20] and the localized orbital [21] methods. By using the notation

$$a_j^{(n+1)} = \sum_k a_k^{(n)} u_{kj}^{(n+1)*}, \tag{12}$$

$$x_{jk}^{(n+1)} = \sum_{lm} u_{lj}^{(n+1)*} x_{lm}^{(n)} u_{mk}^{(n+1)}, \tag{13}$$

and so on, the Hamiltonian is rewritten as

$$H = \sum_j \varepsilon_j^{(1)} a_j^{(1)\dagger} a_j^{(1)} + \frac{1}{4} \sum_{jklm} v_{km}^{jl(1)} a_j^{(1)\dagger} a_l^{(1)\dagger} a_m^{(1)} a_k^{(1)} - \sum_{jk} x_{jk}^{(1)} a_j^{(1)\dagger} a_k^{(1)} - \sum_{\xi\eta} \sum_{jk \in M_{\xi\eta}} y_{jk}^{(1)} a_j^{(1)\dagger} a_k^{(1)}. \tag{14}$$

Of course, successive modifications are possible and to be utilized. For example, putting

$$M_{\xi\eta} = M_{\xi\eta 1} \oplus M_{\xi\eta 2} \oplus \cdots \quad (\xi = 1,2;\, \eta = 1,2,\cdots) \tag{15}$$

and solving

$$\sum_{k \in M_{\xi\eta\zeta}} (\delta_{jk} \varepsilon_j^{(1)} + z_{jk}^{(1)}) u_{kl}^{(2)} = u_{jl}^{(2)} \varepsilon_l^{(2)} \quad (l \in M_{\xi\eta\zeta})(\xi = 1,2;\, \eta,\zeta = 1,2,\cdots), \tag{16}$$

we have

$$H = \sum_j \varepsilon_j^{(2)} a_j^{(2)\dagger} a_j^{(2)} + \frac{1}{4} \sum_{jklm} v_{km}^{jl(2)} a_j^{(2)\dagger} a_l^{(2)\dagger} a_m^{(2)} a_k^{(2)} - \sum_{jk} x_{jk}^{(2)} a_j^{(2)\dagger} a_k^{(2)} - \sum_{\xi\eta} \sum_{jk \in M_{\xi\eta}} y_{jk}^{(2)} a_j^{(2)\dagger} a_k^{(2)} - \sum_{\xi\eta\zeta} \sum_{jk \in M_{\xi\eta\zeta}} z_{jk}^{(2)} a_j^{(2)\dagger} a_k^{(2)}. \tag{17}$$

Presumably it is suitable to call the process of modifications as a whole the MO modification step.

The "smallest" modification is the one-dimensional transformation; the MO does not change but the MO energy does. This is nothing other than level-shifting[22–26] and should be discussed separately from the above mentioned MO modification step. After any MO modification step consisting of g stages we are always still allowed to transform MO's as

$$\varepsilon_j = \varepsilon_j^{(g)} + \theta_j \tag{18}$$

with

$$u_{jk} = \delta_{jk}. \tag{19}$$

To rewrite $a_j^{(g)}$ as a_j, $x_{jk}^{(g)}$ as x_{jk}, and so on leads us to the resultant expression for the partitioned Hamiltonian

$$H = K + V \tag{20}$$

with

$$K = \sum_j \varepsilon_j a_j^\dagger a_j \tag{21}$$

and

$$V = \frac{1}{4} \sum_{jklm} v_{km}^{jl} a_j^\dagger a_l^\dagger a_m a_k - \sum_{jk} x_{jk} a_j^\dagger a_k - \sum_{\xi\eta} \sum_{jk \in M_{\xi\eta}} y_{jk} a_j^\dagger a_k - \sum_{\xi\eta\zeta} \sum_{jk \in M_{\xi\eta\zeta}} z_{jk} a_j^\dagger a_k - \cdots - \sum_j \theta_j a_j^\dagger a_j. \tag{22}$$

Apart from the MO modification step, which is to be based on physical reasoning, we can and should always adjust the MO energies by shifting in order to let the unperturbed Hamiltonian be the "best"; it must be emphasized that this MO energy shift step has nothing to do with the topological nature of the MO at all, as is obviously shown in Eq. 19. In the field of molecular quantum mechanics, the level shifting has been introduced and utilized in connection with the convergence problem in self-consistency procedure from a rather technical standpoint.[23] Another utilization worth referring to is seen in the degenerate perturbation approach.[22,24]

A Variational Determination of the MO Energy Shift

It is not very obvious how to determine the MO energy shift. In this section we describe one possible way of determining the MO energy shift for the canonical HF orbitals (without modification, for brevity), based on the quantum-mechanical variation principle. Hereafter the indices $\{j,k,l,m\}$ and $\{a,b,c,d\}$ are, respectively, used to label the occupied and unoccupied MO's: $j,k,l,m \in M_1$ and $a,b,c,d \in M_2$. The index i labels both: $i \in M$.

Let $|\psi>$ be a trial correlated state corresponding to the Fermi sea state. To take the first order perturbative state correction into account leads us to

$$|\Psi\rangle = (1+C^{\dagger})|F\rangle \tag{23}$$

with

$$C^{\dagger} = -\frac{1}{4}\sum_{abjk} v_{jk}^{ab} w_{jk}^{ab} a_a{}^{\dagger} a_b{}^{\dagger} a_k a_j, \tag{24}$$

where the notation

$$w_{jk}^{ab} = 1/(\varepsilon_a+\varepsilon_b-\varepsilon_k-\varepsilon_j) \tag{25}$$

is used; of course, we have

$$w_{jk}^{ab} = w_{kj}^{ab} = w_{jk}^{ba} = w_{kj}^{ba} \tag{26}$$

and

$$w_{jk}^{ab} = -\, w_{ab}^{jk}. \tag{27}$$

The HF choice (Eq. 7) prevents any singly excited configuration from appearing in the first order state correction.[1] Denoting the exact ground state energy of H by E and abbreviating $\langle F|\cdots|F\rangle$ to $\langle\cdots\rangle$, we see the quantum-mechanical variation principle assert that[27–29]

$$E_0 + E_1 + (E_2+E_3)/(1+s) \geqq E \tag{28}$$

with

$$E_0 + E_1 = \langle K+V\rangle = \sum_j \varepsilon_j^{(0)} - \frac{1}{2}\sum_{jk} v_{jk}^{jk}, \tag{29}$$

$$E_2 = \langle [C,V]\rangle = -\frac{1}{4}\sum_{abjk} |v_{jk}^{ab}|^2 w_{jk}^{ab}, \tag{30}$$

$$\begin{aligned} E_3 &= \langle [[C,V],C^{\dagger}]\rangle \\ &= \frac{1}{8}\sum_{abjk} v_{jk}^{ab} w_{jk}^{ab}\Big(-2(\theta_a+\theta_b-\theta_k-\theta_j) v_{ab}^{jk} w_{jk}^{ab} \\ &\quad + \sum_{cd} v_{ab}^{cd} v_{cd}^{jk} w_{jk}^{cd} + \sum_{lm} v_{lm}^{jk} v_{ab}^{lm} w_{lm}^{ab} + 8\sum_{cl} v_{bl}^{kc} v_{ca}^{lj} w_{lj}^{ca}\Big), \end{aligned} \tag{31}$$

and

$$s = \langle [C,C^{\dagger}]\rangle = \frac{1}{4}\sum_{abjk} |v_{jk}^{ab}|^2 w_{jk}^{ab\,2}. \tag{32}$$

Now since E_0+E_1 is independent of $\{\theta_i\}$, that is,

$$\frac{\partial}{\partial\theta_i}(E_0+E_1) = 0 \quad (\text{any } i), \tag{33}$$

we require the "best" $\{\theta_i\}$ to fulfil the necessary condition

$$\frac{\partial}{\partial\theta_i}\left(\frac{E_2+E_3}{1+s}\right) = 0 \quad (\text{any } i), \tag{34}$$

which gives inhomogeneous simultaneous equations of variation parameters $\{\theta_i\}$. Generally speaking, they are to be solved only numerically, say, with the Newton-Raphson method. Here it should be noted that Eq. 34's for all i are not independent of each other, for the following equation identically holds.

$$\sum_i \frac{\partial}{\partial\theta_i}\left(\frac{E_2+E_3}{1+s}\right) = 0. \tag{35}$$

We can and should set, at least, one of $\{\theta_i\}$ arbitrarily. The quantities needed in the numerical solution are the derivatives of E_2+E_3 and s with respect to $\{\theta_i\}$, which have expression as

$$\begin{aligned} \frac{\partial}{\partial\theta_m}(E_2+E_3) &= \frac{1}{2}\sum_{abj} w_{jm}^{ab\,2}\Big\{-2|v_{jm}^{ab}|^2(\theta_a+\theta_b-\theta_m-\theta_j) w_{jm}^{ab} \\ &\quad + \sum_{cd} \mathrm{Re}(v_{jm}^{ab} v_{ab}^{cd} v_{cd}^{jm}) w_{jm}^{cd} + \sum_{kl} \mathrm{Re}(v_{jm}^{ab} v_{kl}^{jm} v_{ab}^{kl}) w_{kl}^{ab} \\ &\quad + 4\sum_{ck}\big(\mathrm{Re}(v_{jm}^{ab} v_{bk}^{jc} v_{ca}^{mk}) w_{mk}^{ca} + \mathrm{Re}(v_{jm}^{ab} v_{bk}^{mc} v_{ca}^{kj}) w_{kj}^{ca}\big)\Big\}, \end{aligned} \tag{36}$$

$$\begin{aligned} \frac{\partial}{\partial\theta_d}(E_2+E_3) &= -\frac{1}{2}\sum_{ajk} w_{jk}^{ad\,2}\Big\{-2|v_{jk}^{ad}|^2(\theta_a+\theta_d-\theta_k-\theta_j) w_{jk}^{ad} \\ &\quad + \sum_{cd} \mathrm{Re}(v_{jk}^{ad} v_{lm}^{jk} v_{ad}^{lm}) w_{lm}^{ad} + \sum_{bc} \mathrm{Re}(v_{jk}^{ad} v_{ad}^{bc} v_{bc}^{jk}) w_{jk}^{bc} \\ &\quad + 4\sum_{bl}\big(\mathrm{Re}(v_{jk}^{ad} v_{al}^{kb} v_{db}^{lj}) w_{lj}^{db} + \mathrm{Re}(v_{jk}^{ad} v_{dl}^{kb} v_{ba}^{lj}) w_{lj}^{ba}\big)\Big\}, \end{aligned} \tag{37}$$

$$\frac{\partial s}{\partial\theta_m} = \sum_{abj} |v_{jm}^{ab}|^2 w_{jm}^{ab\,3}, \tag{38}$$

and

$$\frac{\partial s}{\partial\theta_d} = -\sum_{ajk} |v_{jk}^{ad}|^2 w_{jk}^{ad\,3}. \tag{39}$$

Note that the quantities dependent on $\{\theta_i\}$ are only $\{w_{jk}^{ab}\}$ besides $\{\theta_i\}$ themselves in the above derivatives. The condition given by Eq. 34 is, of course, not sufficient as the minimum condition, but we have to be contented with describing such stationary one because of practical difficulty; numerical "checking" is possible.

Simplifications by reducing the number of the variation parameters may be worth being investigated. One is to set

$$\begin{cases} \theta_j = \theta & (\text{any } j) \\ \theta_a = \theta' & (\text{any } a), \end{cases} \tag{40}$$

which is actually one-parametric because of Eq. 35; the "distance" between the occupied and unoccupied spaces is arranged as a whole. Another is to use θ_i's only for specific orbitals, say, the highest occupied, the lowest unoccupied, and so on; the number of the variation parameters ranges from one to several. For example,

$$\theta_i = \begin{cases} \theta & (\text{the highest occupied}) \\ \theta' & (\text{the lowest unoccupied}) \\ 0 & \text{otherwise}. \end{cases} \tag{41}$$

Numerical Example

As an illustration we have applied the spin restricted version of the above mentioned methods to the ground state of the helium atom. The result of calculation is summarized in Tables 1, 2, and 3. The canonical HF orbitals are calculated by Roothaan's method[30] using the Slater-type s orbitals

$$\chi = ((2n)!)^{-1/2}(2\zeta)^{n+1/2} r^{n-1} e^{-\zeta r} Y_{00} \tag{42}$$

as a basis. The $1s$ ζ's are taken from best double-ζ calculation by Clementi and Roetti.[31] To the other ζ's we assign $1/n$ without any attempt of optimization.[17]

Table 1. Orbital energy shifts

		Orbital coefficients					Orbital energies and shifts		
ζ		$1s$ 2.91093	$1s$ 1.45363	$2s$ 1/2	$3s$ 1/3	$4s$ 1/4	$\varepsilon^{o\,a)}$	θ	$\varepsilon^{b)}$/a.u.
A1	*1*	0.18069	0.84379				−0.91793		
	d	1.82122	−1.62404				2.82095	−0.67749	2.14346
A2	*1*	0.18086	0.84333	0.00110			−0.91810		
	c	0.03105	−0.30857	1.05129			0.06980	−0.18563	−0.11583
	d	1.91011	−1.78701	0.31414			3.06630	−0.72342	2.34288
A3	*1*	0.18090	0.84324	0.00138	−0.00040		−0.91813		
	b	−0.01332	−0.01401	−0.04517	1.02931		0.01178	−0.18337	−0.17156
	c	0.04443	−0.38961	1.43408	−0.89930		0.11414	−0.19084	−0.07670
	d	1.95601	−1.87274	0.51975	−0.27377		3.18699	−0.74597	2.44102
A4	*1*	0.18092	0.84321	0.00148	−0.00060	0.00019	−0.91814		
	a	0.00182	−0.02688	0.08660	−0.03389	1.00233	0.00406	−0.14505	−0.14099
	b	−0.01873	−0.01689	−0.07767	1.58261	−1.19772	0.02327	−0.18387	−0.16060
	c	0.05325	−0.43548	1.67783	−1.70916	0.81689	0.14095	−0.19761	−0.05666
	d	1.98484	−1.92706	0.66426	−0.56885	0.27001	3.26076	−0.75924	2.50152

a) ε^{o} is the canonical HF orbital energy. b) $\varepsilon=\varepsilon^{o}+\theta$.

Table 2. Correlation corrections

	E_{HF}[a)]	E_c^{o}[b)]	E_c[b)]	ΔE_c[c)]/a.u.
A1	−2.86167	−0.01329	−0.01374	−0.00045
A2	−2.86167	−0.01337	−0.01383	−0.00046
A3	−2.86168	−0.01343	−0.01389	−0.00046
A4	−2.86168	−0.01347	−0.01393	−0.00046

a) $E_{HF}=E_0+E_1$. b) E_c and E_c^{o} are $(E_2+E_3)/(1+s)$ with and without shifting, respectively. c) $\Delta E_c=E_c-E_c^{o}$.

Table 3. One-parameter cases

	θ	E_c[a)]	ΔE_c[a)]/a.u.
A1	−0.67749	−0.01329	−0.00045
B2	−0.42354	−0.01369	−0.00032
B3	−0.38584	−0.01373	−0.00030
B4	−0.37144	−0.01376	−0.00029

a) See the footnote of Table 2.

The unoccupied orbitals are designated as *a, b, c,* and *d* in accordance with the characteristic of the orbital coefficients, the occupied orbital being named *1*. In the cases A1—A4 all of the unoccupied orbital energies are allowed to be variationally shifted, whereas the cases B2—B4 have only one variation parameter common to all the unoccupied orbitals (see Eq. 40); the shift of the occupied orbital energy is set to be zero in every case. Fulfillment of the minimum condition is checked numerically after variational solution for the stationary one.

The values of the orbital energy shifts obtained are neither extraordinary nor negligible. In A1—A4 we have the shifts similar to each other for the corresponding orbitals (the orbitals of the same name), which is the most impressive feature observed from the present example. It is more or less interesting that all the unoccupied orbital energies are shifted low and that the orbital energies of *a* and *b* in A4 are put in the reverse order by shifting. Although these are, of course, to be ascribed to the "nature" of the present example, the inclination reminds us of the hole potential treatment.[17)]

The HF energies in A2—A4 scarcely differ from that of the double-ζ calculation (the HF energy in A1), the changes being 0.00001 a.u.; the correlation corrections with and without shifting, E_c and E_c^{o}, vary clearly as the basis orbitals are added, though by the small amount of 0.00004—0.00009 a.u. On the other hand, the changes of the correlation corrections by shifting are about 0.00046 a.u. in A1—A4 and about 0.00030 a.u. in B2—B4, which are significantly large in comparison with the changes of the HF energies and the correlation corrections by the addition of the basis orbitals. The cases B2—B4 may be said to give passable result, if we take it into account that the method is merely one-parametric.

In spite of poorness of the additional basis, the result obtained here seems rather encouraging. We cannot, however, give any conclusive remark as to how the method proposed in the preceding section work in general. They are to be examined through further numerical calculations on leading systems, which is another enormous story.

Supplementary Remarks

First, we refer to a non-variational way of setting $\{\theta_i\}$. Putting

$$\theta_j = \frac{1}{2}\sum_k v_{jk}^{jk} - x_{jj} - y_{jj} - z_{jj} - \cdots, \tag{43}$$

we have

$$E_0 + E_1 = \sum_j \varepsilon_j. \tag{44}$$

Namely the state energy to first order can be written in terms of a sum of the occupied MO energies without regard to MO coefficients. Thus the Hückel model

Hamiltonian is obtained in a natural way. Especially, under the HF choice with no modification, the HF energy is expressed as

$$E_{\mathrm{HF}} = \sum_{j} \varepsilon_j \tag{45}$$

by setting

$$\theta_j = -\frac{1}{2}\sum_{k} v_{jk}^{jk}, \tag{46}$$

MO coefficients continuing to be the HF ones. The state energy shifting to give the HF energy as the zeroth order state energy has been early devised.[32]

Next, let us consider approximate evaluations of physical quantities with few terms in the Rayleigh-Schrödinger perturbation expansion.[27,28] The perturbation terms contain the MO energy differences in thier energy denominators to second and higher orders, so that the ambiguity due to the MO energy shift is not negligible but may be often significant. We should rather make use of it. Above all, the distance between the occupied and unoccupied spaces is to be treated carefully.

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