On the Molecular Orbital Energy in the Independent-Particle Model

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独立粒子模型における分子軌道エネルギーについて

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Ambiguity in molecular orbital energies is analyzed perturbation-theoretically. It is pointed out that the molecular orbital energy in the independent-particle model is to be adjusted through certain variational condition.

Electronic Structures of Molecules are often well described in terms of the independent-particle model (IPM). It is, however, not very clear how to determine the molecular orbital energy (MOE) ε_i in the IPM Hamiltonian

$$H_{\mathrm{IPM}}=\sum_i \varepsilon_i a_i^\dagger a_i,$$

where $a_i^\dagger$ and a_i are, respectively, the creation and annihilation operators for the molecular orbital (MO) i. One may think that the IPM Hamiltonian is merely a simple sum of the relevant one-particle Hamiltonians used to determine MO's. But the thought is generally incorrect, unless justified by the physical meaning of the one-particle Hamiltonian itself. It seems rather natural to regard the IPM Hamiltonian as the "best" unperturbed Hamiltonian in the perturbation theory for electron correlation.

On the other hand, in investigating the electron correlation problem from a perturbation-theoretical point of view, the following has been noticed: Although the Hartree-Fock(HF) wave function has a physically sound nature as the zeroth order wave function, the so-called HF Hamiltonian is not necessarily a good unperturbed Hamiltonian[1-3].

In this note, analyzing ambiguity in MOE's perturbation-theoretically, we point out that the MOE in the IPM is to be adjusted through certain variational condition.

Let the following second-quantized electronic Hamiltonian be a starting point.

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

where we assume that

$$h_{pq}=h_{qp}^*,$$

$$v_{qs}^{pr} = v_{pr}^{qs*},$$

and

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

Whether the one-electron quantum states $\{p\}$ form a complete set or not, we assume that the space to be considered is defined by the above Hamiltonian.

We go to the MO representation almost always by introducing the HF potential into the eigenvalue problem determining MO's:

$$\sum_q (h_{pq} + \tilde{v}_{pq}) c_{qj} = c_{pj}\varepsilon_j$$

with

$$\tilde{v}_{pq} = \sum_{j\in F} v_{qj}^{pj},$$

where F stands for a set of the occupied orbital indices. The resulting expression of the Hamiltonian is

$$H = \sum_j \varepsilon_j^\circ a_j^+ a_j + \frac{1}{4}\sum_{jklm} v_{km}^{jl} a_j^+ a_l^+ a_m a_k - \sum_{jk} \tilde{v}_{jk} a_j^+ a_k.$$

Since any unitary transformation within the occupied or unoccupied orbital manifold keeps the Fermi sea state

$$|F\rangle = \prod_{j\in F} a_j^+ \,|\, \text{vacuum}\rangle$$

invariant, we can modify MO's, for example, through an eigenvalue problem like[4-6]

$$\sum_{k\in\bar{F}} (\delta_{jk}\varepsilon_j^\circ + y_{jk}) u_{kl} = u_{jl}\varepsilon'_l \qquad (j\in\bar{F}),$$

where $\{y_{jk}\}$ are relevant hermitian matrix elements and $\bar{F}$ stands for a set of the unoccupied orbital indices. The MO indices $\{j, k, \cdots\}$ are used for both the unmodified (old) and modified (new) orbitals, which will bring about no confusion. The Hamiltonian is rewritten as

$$H = \sum_j \varepsilon'_j a_j^+ a_j + \frac{1}{4}\sum_{jklm} v_{km}^{jl} a_j^+ a_l^+ a_m a_k - \sum_{jk} \tilde{v}_{jk} a_j^+ a_k - \sum_{jk\in\bar{F}} y_{jk} a_j^+ a_k - \cdots.$$

After such orbital modifications we still have a room for shifting MOE's;[7]

$$\varepsilon_j = \varepsilon'_j + \theta_j,$$

MO's being left unchanged apart from their energies. Thus the Hamiltonian is partitioned as

$$H = K + V$$

with

$$K = \sum_j \varepsilon_j a_j^+ a_j,$$

and

$$V = \frac{1}{4}\sum_{jklm} v_{km}^{jl} a_j^+ a_l^+ a_m a_k - \sum_{jk} \tilde{v}_{jk} a_j^+ a_k - \sum_{jk\in\bar{F}} y_{jk} a_j^+ a_k - \cdots - \sum_j \theta_j a_j^+ a_j.$$

Regarding H_{IPM} as the "best" K, we are to adjust the MOE's in the above mentioned level-shifting procedure.[8-10]

It is not very obvious, however, how to determine the MOE shift. Here we propose one possible way based on the quantum-mechanical variation principle, confining ourselves to the

shifting for the canonical HF orbital energy for convenience' sake.

Let $|\psi>$ be a trial correlated state corresponding to $|F>$. To take the first order perturbative state correction into account leads us to[11]

$$|\psi>=(1+C^+)|F>$$

with

$$C^+=-\frac{1}{4}\sum_{abjk} v_{jk}^{ab}\xi_{jk}^{ab}a_a^+a_b^+a_ka_j,$$

where

$$\xi_{jk}^{ab}=1/(\varepsilon_a+\varepsilon_b-\varepsilon_k-\varepsilon_j).$$

Hereafter we use indices $\{j, k, \cdots\}$ and $\{a, b, \cdots\}$ to label the occupied and unoccupied orbitals, respectively, whereas only the index i is used unrestrictedly. Let us denote the exact ground state energy of H by E and the expectation value in $|F>$ by the simple bracket. The quantum-mechanical variation principle asserts that[12,13]

$$E_0+E_1+(E_2+E_3)/(1+s)\geqq E$$

with

$$\begin{aligned}
E_0+E_1&=\langle K+V\rangle\\
&=\sum_j(\varepsilon_j^\circ-\tilde{v}_{jj}/2),\\
E_2&=\langle[C,\ V]\rangle\\
&=-\frac{1}{4}\sum_{abjk}|\ v_{jk}^{ab}\ |^2\ \xi_{jk}^{ab},\\
E_3&=\langle[[C,\ V],\ C^+]\rangle\\
&=-\frac{1}{4}\sum_{abjk}|\ v_{jk}^{ab}\ |^2\ (\theta_a+\theta_b-\theta_k-\theta_j)\xi_{jk}^{ab\,2}+\frac{1}{8}\sum_{abcdjk} v_{cd}^{jk}v_{ab}^{cd}v_{jk}^{ab}\xi_{jk}^{cd}\xi_{jk}^{ab}\\
&\quad+\frac{1}{8}\sum_{abjklm} v_{ab}^{lm}v_{lm}^{jk}v_{jk}^{ab}\xi_{lm}^{ab}\xi_{jk}^{ab}-\sum_{abcjkl} v_{bc}^{kl}v_{la}^{jc}v_{jk}^{ab}\xi_{kl}^{bc}\xi_{jk}^{ab},
\end{aligned}$$

and

$$\begin{aligned}
s&=\langle[C,\ C^+]\rangle\\
&=\frac{1}{4}\sum_{abjk}|\ v_{jk}^{ab}\ |^2\ \xi_{jk}^{ab\,2}.
\end{aligned}$$

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

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

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

$$\frac{\partial}{\partial\theta_i}\left(\frac{E_2+E_3}{1+s}\right)=0 \qquad (\text{any } i).$$

This gives inhomogeneous simultaneous equations of variation parameters $\{\theta_i\}$, which are, generally speaking, to be solved only numerically, say, with the Newton-Raphson method. The necessary quantities in the numerical solution are the derivatives of E_2+E_3 and s with respect to $\{\theta_i\}$, which have the following expression:

$$\frac{\partial}{\partial\theta_m}(E_2+E_3)=-\sum_{abj}|\ v_{jm}^{ab}\ |^2\ (\theta_a+\theta_b-\theta_m-\theta_j)\xi_{jm}^{ab\,3}$$

$$+\frac{1}{2}\sum_{abcdj}\mathrm{Re}(v_{cd}^{jm}v_{ab}^{cd}v_{jm}^{ab})\xi_{jm}^{cd}\xi_{jm}^{ab2}+\frac{1}{2}\sum_{abjkl}\mathrm{Re}(v_{ab}^{lm}v_{lm}^{jk}v_{jk}^{ab})\xi_{lm}^{ab2}\xi_{jk}^{ab}$$

$$-2\sum_{abcjk}\left(\mathrm{Re}(v_{bc}^{mk}v_{ka}^{jc}v_{jm}^{ab})\xi_{mk}^{bc}\xi_{jm}^{ab2}+\mathrm{Re}(v_{bc}^{km}v_{ma}^{jc}v_{jk}^{ab})\xi_{km}^{bc2}\xi_{jk}^{ab}\right),$$

$$\frac{\partial}{\partial\theta_d}(E_2+E_3)=\sum_{ajk}|\,v_{jk}^{ad}\,|^2\,(\theta_a+\theta_d-\theta_k-\theta_j)\xi_{jk}^{ad3}$$

$$-\frac{1}{2}\sum_{ajklm}\mathrm{Re}(v_{ad}^{lm}v_{lm}^{jk}v_{jk}^{ad})\xi_{lm}^{ad}\xi_{jk}^{ad2}-\frac{1}{2}\sum_{abcjk}\mathrm{Re}(v_{cd}^{jk}v_{ab}^{cd}v_{jk}^{ab})\xi_{jk}^{cd2}\xi_{jk}^{ab}$$

$$+2\sum_{abjkl}\left(\mathrm{Re}(v_{db}^{kl}v_{la}^{jb}v_{jk}^{ad})\xi_{kl}^{db}\xi_{jk}^{ad2}+\mathrm{Re}(v_{bd}^{kl}v_{la}^{jd}v_{jk}^{ab})\xi_{kl}^{bd2}\xi_{jk}^{ab}\right),$$

$$\frac{\partial S}{\partial\theta_m}=\sum_{abj}|\,v_{jm}^{ab}\,|^2\,\xi_{jm}^{ab3},$$

and

$$\frac{\partial S}{\partial\theta_d}=-\sum_{ajk}|\,v_{jk}^{ad}\,|^2\,\xi_{jk}^{ad3}.$$

Note that the quantities dependent on $\{\theta_i\}$ are only $\{\xi_{jk}^{ab}\}$ besides $\{\theta_i\}$ in the above derivatives.

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

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

which is actually one-parametric; 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,

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

Unfortunately, we cannot give any conclusive remark as to how the above mentioned methods work before numerical investigatory calculations on leading actual systems, which is another enormous story.

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(Received November 1, 1982)