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A Hypervirial Theorem Aspect of Koopmans' Theorem

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Koopmans' theorem is interpreted as a hypervirial theorem requirement; the implication of Koopmans' theorem is thereby clarified. A hypervirial theorem standpoint gives a physically sound ground to a leading correction of Koopmans' relation. Attention is paid to the orbital ambiguity associated with the correction, a possible utilization of the ambiguity being suggested.

Koopmans' theorem¹⁾ is one of the most important characteristics of the standard Hartree-Fock(HF) method,²⁾ giving a definite physical meaning to occupied canonical HF orbitals. However, what is implied in the theorem does not seem to be fully recognized; a well-known approximate evaluation of the vertical ionization energy

$$I_i = -\varepsilon_i^\circ \quad (\varepsilon_i^\circ\text{: }i\text{th canonical HF orbital energy}) \tag{1}$$

is rather misleadingly referred to as Koopmans' theorem.³⁾⁴⁾ In this paper Koopmans' theorem is examined from the viewpoint of the hypervirial theorem(HVT),⁵⁾ which leads us not only to transparent understanding of a nature of Koopmans' theorem but also to a physically sound ground for a leading correction to Koopmans' relation.

Preliminaries

Let us start with writing the Hamiltonian for a system of electrons in a fixed nuclear framework as

$$H = \sum_{\xi\eta} h_{\xi\eta} a_\xi^\dagger a_\eta + \frac{1}{2}\sum_{\xi\eta\theta\gamma} v_{\eta\gamma}^{\xi\theta} a_\xi^\dagger a_\theta^\dagger a_\gamma a_\eta, \tag{2}$$

where $a_\xi^\dagger$ and a_ξ are, respectively, the creation and annihilation operators for the one-particle quantum state ξ. Taking a relevant hermitian one-particle operator

$$X = \sum_{\xi\eta} x_{\xi\eta} a_\xi^\dagger a_\eta,$$

which is to be determined later, going through an eigenvalue problem

$$\sum_\eta (h_{\xi\eta} + x_{\xi\eta}) u_{\eta j} = u_{\xi j}\varepsilon_j, \tag{3}$$

we rewrite Eq. 2 in the molecular orbital representation as

$$H = K + V^{(1)} + V^{(2)} \tag{4}$$

with

$$K = \sum_j \varepsilon_j a_j^\dagger a_j, \tag{5}$$

$$V^{(1)} = -\sum_{jk} x_{jk} a_j^\dagger a_k, \tag{6}$$

and

$$V^{(2)} = \frac{1}{2}\sum_{jklm} v_{km}^{jl} a_j^\dagger a_l^\dagger a_m a_k. \tag{7}$$

Postulating that an eigenstate $|\psi\rangle$ of H is attainable from the corresponding unperturbed eigenstate $|\phi\rangle$ of K through a unitary transformation:

$$|\psi\rangle = \exp(S)|\phi\rangle, \tag{8}$$

where S is an antihermitian operator independent of state indices, we expand S perturbation-theoretically as

$$S = S_1^{(1)} + S_1^{(2)} + \text{ second and higher orders}$$

with

$$S_1^{(1)} = \sum_{jk} s_{jk} a_j^\dagger a_k \tag{9}$$

and

$$S_1^{(2)} = \frac{1}{2}\sum_{jklm} s_{km}^{jl} a_j^\dagger a_l^\dagger a_m a_k. \tag{10}$$

Then the first order one-particle HVT⁵⁾ affirms that

$$\sum_j (y_{jp}\langle a_j^\dagger a_q\rangle - y_{qj}\langle a_p^\dagger a_j\rangle + \sum_{kl} (y_{pl}^{jk}\langle a_j^\dagger a_k^\dagger a_l a_q\rangle - y_{jl}^{qk}\langle a_p^\dagger a_k^\dagger a_l a_j\rangle)) = 0 \quad (\text{any } p, q) \tag{11}$$

with

$$y_{jk} = -x_{jk} + (\varepsilon_j - \varepsilon_k) s_{jk} \tag{12}$$

and

$$y_{km}^{jl} = v_{km}^{jl} + (\varepsilon_j + \varepsilon_l - \varepsilon_m - \varepsilon_k) s_{km}^{jl}, \tag{13}$$

the simple bracket $\langle\cdots\rangle$ in Eq. 11 standing for the expectation value in $|\phi\rangle$. We confine ourselves to single-configurational $|\phi\rangle$'s in the following.

Koopmans' Theorem

First the case without S is considered. Denoting the N-electron Fermi sea state of K by $|F\rangle$:

$$|F\rangle = a_N^\dagger \cdots a_2^\dagger a_1^\dagger |\text{vacuum}\rangle, \tag{14}$$

and sets of the occupied and unoccupied orbitals by F and $\bar{F}$ respectively, we can write the one-particle HVT for the ground state $|F\rangle$ as

$$\langle F|[H, a_p^\dagger a_q]|F\rangle = 0 \qquad (\text{any } p, q) \tag{15}$$

and that for the ionized state $a_i|F\rangle$ $(i\epsilon F)$ as

$$\langle F|a_i^\dagger [H, a_p^\dagger a_q] a_i|F\rangle = 0 \quad (\text{any } p, q). \tag{16}$$

By making use of Eqs. 11, 12, and 13 with all s_{jk}'s and s_{km}^{jl}'s vanishing, Eqs. 15 and 16 are easily converted into

$$(-x_{qp} + \tilde{v}_{qp})(\mathrm{f}(q) - \mathrm{f}(p)) = 0 \tag{17}$$

and

$$(-x_{qp} + \tilde{v}_{qp} - v(i)_{qp})(\mathrm{f}(q) - \mathrm{f}(p) - \delta_{iq} + \delta_{ip}) = 0 \tag{18}$$

respectively, where we introduce the occupation indicator

$$\mathrm{f}(j) = \begin{cases} 1 & (j\epsilon F) \\ 0 & (j\epsilon \bar{F}) \end{cases} \tag{19}$$

and the abbreviations

$$t(l)_{jk} = t_{kl}^{jl} - t_{lk}^{jl}$$

and

$$\tilde{t}_{jk} = \sum_{l\epsilon F} t(l)_{jk}.$$

While Eq. 17 gives the HF condition[5)]

$$x_{jk} = \tilde{v}_{jk} \qquad (j\epsilon F,\ k\epsilon \overline{F},\ \text{and } \textit{vice versa}), \tag{20}$$

Eq. 18 results in

$$\begin{cases} x_{ij} = \tilde{v}_{ij} \text{ and } x_{ji} = \tilde{v}_{ji} \qquad (j\epsilon F') & (21) \\ v(i)_{jk} = 0 \qquad (j\epsilon F',\ k\epsilon \overline{F},\ \text{and } \textit{vice versa}) & (22) \end{cases}$$

with Eq. 20 assumed, the prime on F indicating the exclusion of i: $F'=F-\{i\}$. Since we cannot satisfy Eq. 22 in general, Eqs. 15 and 16 are intrinsically prevented from holding simultaneously.

Now for the ionized state, contented with the HVT in a restricted region

$$\langle F|a_i^\dagger[H, a_p^\dagger a_q]a_i|F\rangle = 0 \qquad (p, q\epsilon F,\ \text{and } p, q\epsilon \overline{F}') \tag{23}$$

with $\overline{F}'=\overline{F}+\{i\}$, we are free from Eq. 21; the two HVT's, Eqs. 15 and 23 are compatible with each other and lead together to

$$x_{jk} = \tilde{v}_{jk} \quad (j\epsilon F, k\epsilon \overline{F} \text{ and } \textit{vice versa};\ j, k\epsilon F,\ j \text{ or } k=i). \tag{24}$$

Thus we see a HVT aspect of Koopmans' theorem: When the molecular orbitals are determined so as to satisfy Eq. 24, a single-configurational approximation of the vertical ionization energy

$$\begin{aligned} I_i &= \langle F|a_i^\dagger H a_i|F\rangle - \langle F|H|F\rangle \\ &= -h_{ii} - \tilde{v}_{ii} \end{aligned} \tag{25}$$

is at its best.

Conversely, we can formally make Eq. 16 compatible with the ground state HVT in a restricted region. This coalition is, however, unnatural and disadvantageous, as long as the matrix elements $\{h_{\xi\eta}\}$ and $\{v_{\eta\gamma}^{\xi\theta}\}$ are set to be appropriate to the more stable ground state.

A sufficient way to satisfy Eq. 24 is obviously to put

$$x_{jk} = \tilde{v}_{jk} \qquad (\text{any } j, k) \tag{26}$$

or in the initial representation

$$x_{\xi\eta} = \sum_{\theta\gamma} (v_{\eta\gamma}^{\xi\theta} - v_{\gamma\eta}^{\xi\theta})\rho_{\gamma\theta} \tag{27}$$

with

$$\rho_{\gamma\theta} = \sum_{j\epsilon F} u_{\gamma j} u_{\theta j}^*. \tag{28}$$

The eigenvalue problem obtained by substituting Eq. 27 into Eq. 3 can be solved with Eq. 28 self-consistently, giving the canonical HF orbitals. If canonical HF orbitals are used, we can rewrite Eq. 25 as Eq. 1. This step is, however, just only rewriting of no physical content.[6)] It seems to be desired to call Eq. 1 itself not Koopmans' theorem but relation.

It should be emphasized that Eq. 24 leaves many of x_{jk}'s for $j,k\epsilon F$ and all x_{jk}'s for $j,k\epsilon \overline{F}$ undetermined. This ambiguity is to be utilized purposively. We can require Eq. 23 consistently for all $i\epsilon F$ besides Eq. 15, if necessary, the resultant condition being

$$x_{jk} = \tilde{v}_{jk} \quad (j\epsilon F, k\epsilon \overline{F} \text{ and } \textit{vice versa};\ j, k\epsilon F, j\neq k). \tag{29}$$

We have Eq. 26 again as a sufficient choice of X. It is worth while to note that x_{jj}'s remain still undetermined even for $j\epsilon F$ in Eq. 29. Since all x_{jk}'s for $j,k\epsilon \overline{F}$ are not conditioned in Eq. 24, Koopmans' theorem is valid in the hole potential method.[5,7)] The electron-hole potential choice of X is generally inconsistent with Eq. 24.[5,8)]

A Leading Correction to Koopmans' Relation

Next let us consider to fulfil the one-particle HVT's for the ground and ionized states,

$$\langle F|\exp(-S)[H, a_p^\dagger a_q]\exp(S)|F\rangle = 0 \qquad (\text{any } p, q) \tag{30}$$

and

$$\langle F|a_i^\dagger \exp(-S)[H, a_p^\dagger a_q]\exp(S)a_i|F\rangle = 0 \qquad (\text{any } p, q), \tag{31}$$

simultaneously to first order by using simple S. Putting $|\phi\rangle=|F\rangle$ and $|\phi\rangle=a_i|F\rangle$ in Eq. 11 respectively, we immediately obtain

$$(y_{qp}+\tilde{y}_{qp})(\mathrm{f}(q)-\mathrm{f}(p)) = 0 \tag{32}$$

and

$$(y_{qp}+\tilde{y}_{qp}-y(i)_{qp})(\mathrm{f}(q)-\mathrm{f}(p)-\delta_{iq}+\delta_{ip}) = 0. \tag{33}$$

The former gives

$$-y_{jk} = \tilde{y}_{jk} \qquad (j\epsilon F, k\epsilon \overline{F},\ \text{and } \textit{vice versa}), \tag{34}$$

letting the latter result in

$$\begin{cases} -y_{ij} = \tilde{y}_{ij} \text{ and } -y_{ji}=\tilde{y}_{ji} \qquad (j\epsilon F') & (35) \\ y(i)_{jk} = 0 \qquad (j\epsilon F', k\epsilon \overline{F},\ \text{and } \textit{vice versa}). & (36) \end{cases}$$

Forming a striking contrast to Eqs. 22 and 36 merely asserts that

$$s(i)_{jk} = v(i)_{jk}/(\varepsilon_k-\varepsilon_j) \quad (j\epsilon F', k\epsilon \overline{F},\ \text{and } \textit{vice versa}). \tag{37}$$

The other s_{km}^{il}'s are allowed to be zero. We have alternatives with regard to fulfilment of Eq. 34.

If we make all s_{jk}'s vanishing, Eq. 34 becomes

$$x_{jk} = \tilde{v}_{jk} - v(i)_{jk} \qquad (j\epsilon F, k\epsilon \overline{F},\ \text{and } \textit{vice versa}) \tag{38}$$

by virtue of Eq. 37. From Eq. 35 we have

$$x_{ij} = \tilde{v}_{ij} \text{ and } x_{ji} = \tilde{v}_{ji} \qquad (j\epsilon F'). \tag{39}$$

Because $v(i)_{ij}$ and $v(i)_{ji}$ vanish identically for any j, Eqs. 38 and 39 can be achieved by the standard HF calculation for the ionized configuration. There is no first order correction to the ionized state; we have

$$S_1^{(2)}|F\rangle = \sum_{j\epsilon \overline{F},\, k\epsilon F'} v(i)_{jk}/(\varepsilon_k-\varepsilon_j)a_j^\dagger a_k|F\rangle. \tag{40}$$

The resultant approximation of the vertical ionization energy is, to second order, given by

$$I_i = -h_{ii} - \tilde{v}_{ii} + \sum_{j\epsilon \overline{F},\, k\epsilon F'} |v(i)_{jk}|^2/(\varepsilon_j-\varepsilon_k). \tag{41}$$

Note that x_{jk}'s for $j,k\epsilon F'$ and $j,k\epsilon \overline{F}$ are not conditioned in Eqs. 38 and 39; Eq. 41 remains ambiguous.

Another way, usually fitting real situations better than the preceding, consists in adhering to the ground state HF condition, Eq. 20. In consequence it follows from Eq. 34 that

$$s_{jk} = v(i)_{jk}/(\varepsilon_j-\varepsilon_k) \quad (j\epsilon F, k\epsilon \overline{F},\ \textit{vice versa}) \tag{42}$$

after substitution of Eq. 37. The other s_{jk}'s can be set to vanish; we have Eq. 39 as before from Eq. 35. This time the first order state correction does not appear in the ground state, but does in the ionized:

$$(S_1^{(1)}+S_1^{(2)})a_i|F\rangle = \sum_{j\epsilon \overline{F},\, k\epsilon F'} v(i)_{jk}/(\varepsilon_j-\varepsilon_k)a_j^\dagger a_k a_i|F\rangle. \tag{43}$$

Accordingly, in place of Eq. 41, we have

$$I_i = -h_{ii} - \tilde{v}_{ii} - \sum_{j\in\bar{F},\, k\in F'} |v(i)_{jk}|^2/(\varepsilon_j - \varepsilon_k). \tag{44}$$

Again it should be noted that the ambiguity in x_{jk}'s for $j,k\in F'$ and $j,k\in\bar{F}$ leaves Eq. 44 undetermined. Although how to utilize this ambiguity is not very evident, it seems much more plausible to use the orbitals satisfying

$$x_{jk} = \tilde{v}_{jk} - v(i)_{jk} \qquad (j,\, k\in F' \text{ and } j,\, k\in\bar{F}) \tag{45}$$

rather than to hold on the canonical HF orbitals for the ground state configuration; the second order term in Eq. 44 exclusively comes from the correction concerning the ionized state.

In order to have Eqs. 20, 39, and 45 hold, it is sufficient to take X as

$$x_{jk} = \tilde{v}_{jk} - \mathrm{f}(j)v(i)_{jk}\mathrm{f}(k) - (1-\mathrm{f}(j))v(i)_{jk}(1-\mathrm{f}(k)). \tag{46}$$

Denoting the one-particle quantum state by the round bra and ket, we employ the projection operators7)

$$\mathrm{P} = \sum_j |j)\mathrm{f}(j)(j| \tag{47}$$

and

$$\bar{\mathrm{P}} = \sum_j |j)(1-\mathrm{f}(j))(j|, \tag{48}$$

which are invariant under unitary transformations within each of the orbital subsets F and $\bar{F}$. With the abbreviations

$$\rho_{\xi\eta} = (\xi|\mathrm{P}|\eta) = \sum_{j\in F} u_{\xi j}u^*_{\eta j} \tag{49}$$

and

$$\bar{\rho}_{\xi\eta} = (\xi|\bar{\mathrm{P}}|\eta) = \sum_{j\in\bar{F}} u_{\xi j}u^*_{\eta j} \tag{50}$$

we can rewrite Eq. 46 in the initial representation as

$$x_{\xi\eta} = \sum_{\theta\gamma} ((v^{\xi\theta}_{\eta\gamma} - v^{\xi\theta}_{\gamma\eta})\rho_{\gamma\theta} - \rho_{\xi\theta}v(i)_{\theta\gamma}\rho_{\gamma\eta} - \bar{\rho}_{\xi\theta}v(i)_{\theta\gamma}\bar{\rho}_{\gamma\eta}). \tag{51}$$

However, to solve Eq. 3 with Eqs. 49, 50, and 51 seems unreasonably inefficient. A stepwise method is practical: First perform the standard HF calculation for the ground state configuration to obtain the canonical HF orbitals $\{\underline{j}\}$ and their energies $\{\varepsilon_{\underline{j}}\}$. Selecting a relevant occupied orbital $\underline{i}$, next work out the two separate eigenvalue problems

$$\sum_{\underline{l}\in F'} (\delta_{\underline{k}\underline{l}}\varepsilon_{\underline{k}} - v(\underline{i})_{\underline{k}\underline{l}})c_{\underline{l}j} = c_{\underline{k}j}\varepsilon_j \qquad (\underline{k}\in F') \tag{52}$$

and

$$\sum_{\underline{l}\in\bar{F}} (\delta_{\underline{k}\underline{l}}\varepsilon_{\underline{k}} - v(i)_{\underline{k}\underline{l}})c_{\underline{l}j} = c_{\underline{k}j}\varepsilon_j \qquad (\underline{k}\in\bar{F}), \tag{53}$$

which give rise to the new orbitals $\{j\}$ with their energies $\{\varepsilon_j\}$, the orbital i being identical with $\underline{i}$. No iterative procedure for self-consistency is involved in solving Eqs. 52 and 53.

The simultaneous fulfilment of the one-particle HVT's for the ground and ionized states leads us to taking it into account the effect of the charge distribution rearrangement through ionization.9)

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