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# Hartree–Fock Equation for Hole States: Extension of the Variational Meaning of Koopmans' Theorem to Many–Electron Ionization

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# Hartree–Fock Equation for Hole States: Extension of the Variational Meaning of Koopmans' Theorem to Many–Electron Ionization[#]

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**Abstract**

**Motivation.** Koopmans' theorem not only provides a numerical method to calculate approximate ionization potential energies but also has another variational meaning. We have shown that an extension of the variational meaning of the theorem to many–electron ionization processes leads naturally to the SCF equation for hole orbitals.

**Results.** In this paper the Hartree–Fock equation for hole states is derived using the variational method.

**Conclusions.** The variational meaning of Koopmans' theorem has been extended to many–electron ionization processes. The obtained equation corresponds to the Hartree–Fock equation for hole states. Koopmans' theorem has been recognized as one of the expressions of the general variational duality between the electronic and the hole states.

**Keywords.** Koopmans' theorem; Hartree–Fock; hole orbitals; variational duality.

| **Abbreviations and notations** | |
|---|---|
| H–F, Hartree–Fock | SCF, self–consistent field |

## 1 INTRODUCTION

In quantum chemistry calculations, Koopmans' theorem [1] has often been applied to calculate ionization potential energies based on the frozen–orbital approximation [2,3]. It is well known, however, that the theorem has another variational meaning that one–electron ionized states are already optimized energetically within the occupied orbitals of Hartree–Fock (H–F) wave functions of parent atoms or molecules [1,4]. In this work, we show that an extension of the variational meaning of the theorem to many–electron ionization processes leads naturally to the SCF (self–consistent field) equation for hole orbitals. By introducing a virtual hole–state wave function, the

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variational duality between the electronic and the hole states is shown explicitly. The variational meaning of Koopmans' theorem is recognized as one of the expressions of this variational duality.

## 2 EXTENSION OF KOOPMANS' THEOREM TO MANY–ELECTRON IONIZATION

We first consider an *Ne*–electron system which is generated by *Nh*–electron ionization from an *N*–electron system: *Ne* = *N* – *Nh*. The H–F wave function for the parent *N*–electron system is expressed with a normalized Slater determinant of spin orbitals $\chi_i^0$,

$$\Psi_N^0 = \| \chi_1^0 \chi_2^0 \cdots \chi_i^0 \cdots \chi_N^0 \|. \tag{1}$$

We assume that the spin orbitals of the *Ne*–electron system, $\chi_a$, are obtained variationally within the submanifold of *N* spin orbitals of the parent system using the unitary transformation as the variational freedom,

$$\Psi_{Ne} = \| \chi_1 \chi_2 \cdots \chi_a \cdots \chi_{Ne} \|, \tag{2}$$

where

$$\chi_a = \sum_{i=1}^{N} \chi_i^0 U_{ia}, \qquad (a = 1, 2, \cdots, Ne), \tag{3}$$

$$\chi_r = \sum_{i=1}^{N} \chi_i^0 U_{ir}, \qquad (r = Ne+1, \ Ne+2, \cdots, Ne+Nh). \tag{4}$$

Here, as indexes of orbitals, *a* or *b* is used for the *Ne*–electron system, *r* or *s* for the ionizing *Nh*–electron system, and *i* or *j* runs over the all orbitals of the parent *N*–electron system. The electronic energy of the *Ne*–electron system is calculated as

$$
\begin{aligned}
E^{Ne} &= <\Psi_{Ne} | H^{Ne} | \Psi_{Ne}> = \sum_a^{Ne} <\chi_a | h | \chi_a> + \sum_{a<b}^{Ne} <\chi_a \chi_b \| \chi_a \chi_b> \\
&= \sum_i^{N} <\chi_i | h | \chi_i> + \sum_{i<j}^{N} <\chi_i \chi_j \| \chi_i \chi_j> \\
&\quad - \sum_r^{Nh} <\chi_r | h | \chi_r> - \sum_r^{Nh} \sum_i^{N} <\chi_r \chi_i \| \chi_r \chi_i> + \sum_{r<s}^{Nh} <\chi_r \chi_s \| \chi_r \chi_s> \\
&= <\Psi_N | H^N | \Psi_N> - \sum_r^{Nh} <\chi_r | h + \sum_i^{N} (J_i - K_i) | \chi_r> + \sum_{r<s}^{Nh} <\chi_r \chi_s \| \chi_r \chi_s> \\
&= E^N - \sum_r^{Nh} <\chi_r | f^N | \chi_r> + \sum_{r<s}^{Nh} <\chi_r \chi_s \| \chi_r \chi_s> \\
&= E_0^N - \left[ \sum_r^{Nh} <\chi_r | f_0^N | \chi_r> - \sum_{r<s}^{Nh} <\chi_r \chi_s \| \chi_r \chi_s> \right],
\end{aligned}
\tag{5}
$$

where $H^{Ne}$ and $H^N$ are usual electronic Hamiltonian operators for *Ne*– and *N*–electron systems,

respectively. The operator $f^N$ is the Fock operator for the $N$–electron system and $<\chi_i \chi_j \| \chi_i \chi_j> = <\chi_i \chi_j | \chi_i \chi_j> - <\chi_i \chi_j | \chi_j \chi_i>$. The following unitary invariance

$$E^N = E_0^N, \qquad f^N = f_0^N, \tag{6}$$

for the transformations (3) and (4), is also used.

The $Nh$–electron ionization potential energy, $I_P^{Nh}$, is calculated as

$$-I_P^{Nh} = E_0^N - E^{Ne} = \sum_r^{Nh} <\chi_r | f_0^N | \chi_r> - \sum_{r<s}^{Nh} <\chi_r \chi_s \| \chi_r \chi_s>. \tag{7}$$

In Eq. (7), $E_0^N$ is constant for the unitary transformation and the extremum condition for $E^{Ne}$ is equivalent to that for $I_P^{Nh}$.

Koopmans' theorem corresponds to the case of $Nh = 1$. In Eq. (7), $<\chi_r \chi_s \| \chi_r \chi_s>$ terms will not appear and the extremum condition for $E^{Ne}$ results in the eigenvalue problem for $f_0^N$. So the H–F canonical orbitals, $\chi_i^0$, of $N$–electron systems satisfy the extremum condition for $E^{Ne}$. This is the variational meaning of Koopmans' theorem. Ionization potential energies become the orbital energies of the parent $N$–electron systems in the opposite sign.

In the case of $Nh \geq 2$, the two–electron terms should be considered in the variational process. In the next section, this leads newly to the SCF equation for the $Nh$ orbitals which correspond to the hole orbitals of the $Ne$–electron system.

## 3 SCF EQUATION

By extending the variational meaning of Koopmans' theorem to many–electron ionization processes, we derive the SCF equation for $Nh$ hole orbitals. Here we consider the extremum condition for $(-I_P^{Nh})$ in Eq. (7) with the orthogonality condition of $\chi_r$ orbitals. The functional for the variation is defined by

$$L = (-I_P^{Nh}) - \sum_r^{Nh} \sum_s^{Nh} \lambda_{sr} (<\chi_r | \chi_s> - \delta_{rs}), \tag{8}$$

and the extremum condition is written as

$$\delta L = \sum_r^{Nh} <\delta\chi_r | \left\{ \left[ f_0^N - \sum_s^{Nh} (J_s - K_s) \right] | \chi_r> - \sum_s^{Nh} \lambda_{sr} | \chi_s> \right\} + complex\ conjugate = 0, \tag{9}$$

with $\lambda_{sr} = \lambda_{rs}^*$. For arbitrary variation $\delta\chi_r$, we obtain

$$\left[ f_0^N - \sum_s^{Nh} (J_s - K_s) \right] | \chi_r> = \sum_s^{Nh} \lambda_{sr} | \chi_s>. \tag{10}$$

If we define the Fock operator for the hole orbitals as

$$F_{hole}^{Nh} = f_0^N - \sum_s^{Nh} (J_s - K_s),$$
(11)

the SCF Eq. (10) is rewritten as

$$F_{hole}^{Nh} | \chi_r >= \sum_s^{Nh} \lambda_{sr} | \chi_s >.$$
(12)

The SCF Eq. (12), constructed with only hole orbitals $\chi_r$, may be efficient numerically when the convergence of the occupied orbitals of the *Ne*–electron system is slower.

## 4 H–F EQUATION FOR VIRTUAL HOLE–STATE WAVE FUNCTION

As shown in Figure 1, next we introduce a virtual hole–state wave function, $\Psi_{Nh}^{hole}$, which will lead to the SCF Eq. (12) as the H–F equation for the hole state.
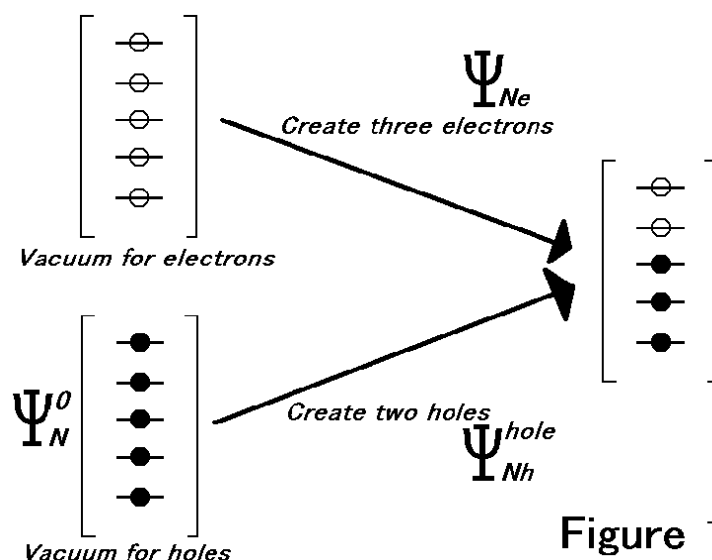


**Figure 1.** The duality between the electronic state $\Psi_{Ne}$ and the hole state $\Psi_{Nh}^{hole}$.

The *Nh*–hole–state wave function is constructed with only the hole orbitals $\chi_r$

$$\Psi_{Nh}^{hole} = \| \chi_1 \chi_2 \cdots \chi_r \cdots \chi_{Nh} \|.$$
(13)

By using the Fock operator $f_0^N$ as a "core–Hamiltonian", the hole–state Hamiltonian is defined as

$$H_{hole}^{Nh} = \sum_r^{Nh} f_0^N (x_r) - \sum_{r<s}^{Nh} \frac{1}{|x_r - x_s|}.$$
(14)

Formally, the coulombic interaction has the negative sign as well as in Eq. (11). The total energy of the *Nh*–hole–state is calculated as

$$E_{hole}^{Nh} = < \Psi_{Nh}^{hole} | H_{hole}^{Nh} | \Psi_{Nh}^{hole} >= \sum_r^{Nh} < \chi_r | f_0^N | \chi_r > - \sum_{r<s}^{Nh} < \chi_r \chi_s \| \chi_r \chi_s >= -I_P^{Nh}.$$
(15)

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From this equality of $E_{hole}^{Nh}$ and $(-I_P^{Nh})$, the SCF equation (12) will be obtained immediately by adopting the variational method for the *Nh*–hole–state wave function $\Psi_{Nh}^{hole}$ in Eq. (13). The SCF equation (12) is now identified as the H–F equation for the hole state (13). Moreover, from Eqs. (7) and (15), we have:

$$E_0^N = E^{Ne} + E_{hole}^{Nh}. \tag{16}$$

So the sum of the electronic energy $E^{Ne}$ and the hole–state energy $E_{hole}^{Nh}$ is constant and the minimum condition for one is the maximum for the other. This is the variational duality between the electronic–state wave function $\Psi_{Ne}$ and the hole–state wave function $\Psi_{Nh}^{hole}$ as shown in Figure 1. Koopmans' theorem, *Nh* = 1 in Eq. (7), can be recognized as one of the expressions of this variational duality between the electronic and the hole states.

As a numerical example, H–F energies are calculated for $H_2O$ with STO–3G minimal basis set at its optimized geometry. There are two hole space–orbitals in the spin–restricted approximation. The neutral molecule $H_2O$ is calculated by ionizing four electrons from $H_2O^{4-}$. The obtained energies are $E_0^N = E_{H_2O^{4-}} = -78.078246 \, au$, $E^{Ne} = E_{H_2O} = -83.872589 \, au$, and $E_{hole}^{Nh} = 5.794343 \, au$ where nuclear repulsion energy $8.906688 \, au$ is not included.

# 5 CONCLUSIONS

The variational meaning of Koopmans' theorem has been extended to many–electron ionization processes. The obtained variational equation is the SCF equation for hole orbitals. By introducing the wave function and the Hamiltonian operator for the virtual hole–state, the SCF equation is identified as the hole–state H–F equation. Although the equations of the hole states may not be so useful for practical calculations, they show explicitly the variational duality between the electronic and the hole states. Koopmans' theorem is recognized as one of the expressions of this general variational duality.

# 6 REFERENCES

[1]  T. Koopmans, Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen eines Atoms, *Physica* **1933**, *1*, 104–113.
[2]  H. F. Schaefer III (Ed.), *Applications of Electronic Structure Theory*, Plenum, New York, 1977.
[3]  X. –Y. Li, X.–S. Tang, and F. –C. He, Electron transfer in poly(p–phenylene) oligomers: effect of external electric field and application of Koopmans theorem, *Chem. Phys.* **1999**, *248*, 137–146.
[4]  M. D. Newton, Analysis of Koopmans' Theorem, *J. Chem. Phys.* **1968**, *48*, 2825–2826.