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On the Simple Energy Relation Between the RHF, UHF and Closed-Shell SCF Methods

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The simple energy relation between the RHF and UHF methods are obtained by expanding these orbital sets by the closed-shell orbital with the same geometry of the open-shell systems. The results are also applied to higher spin states.

Key words: Energy relation – RHF – UHF – closed shell SCF.

It is well known that the restricted Hartree–Fock (RHF) method proposed by Roothaan [1] and the unrestricted Hartree–Fock (UHF) method of Pople and Nesbet [2] are two powerful methods for the study of open-shell systems. Since the pioneer study by Amos and Hall [3], the relations between these two methods have been extensively discussed by several authors especially with respect to their spin-density properties [3, 6]. In this study, we give a simple method to clarify the connection of their energy properties, namely the relation between the ionization energies or electron affinities obtained by the RHF and UHF methods. In our treatment, the RHF and UHF orbital sets are expanded by the closed-shell orbital with the same geometry of the open-shell systems and these expansion coefficients

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are used to analyze the difference of the orbital energies or the total energies by the RHF and UHF methods. Using the same closed-shell orbital in this expansion, we can obtain the clearer and simpler energy relation between these two methods and also recognize their important characteristics.

Here the original open-shell orbitals $\{i^x\}$ are expanded by the orbital sets of the closed-shell system $\langle i|^1$,

$$\{i^x\} = a^x_{ii} < i| + \sum_{i \neq j}^{\text{occ}} a^x_{ij} < i| + \sum_{k}^{\text{vac}} a^x_{ik} < k| + a^x_{im} < m|, \qquad (x; R, \alpha \text{ and } \beta) \tag{1}$$

where $\{i^R\}$, $\{i^\alpha\}$ and $\{i^\beta\}$ denote the RHF orbital set and the α-spin and β-spin orbital sets of the UHF method, respectively. The indices i and j refer to the occupied orbitals in the closed- and open-shell systems, m to the unoccupied orbitals in the closed-shell system, whereas the odd electron in the open-shell system, and k and l to the vacant orbitals in both systems. These notations are valied only for anion radicals in case the closed-shell systems mean neutral molecules. For cation radicals, the indice m means the occupied orbital in the closed-shell system. After a relevant transformation [4] which diagonalizes the matrix a_{ij}, we obtain with an appropriate normalization,

$$\langle i^x| = \langle i| + \sum_{k}^{\text{vac}} \lambda^x_{ik} \langle k| + \lambda^x_{im} \langle m|. \tag{2}$$

By way of example, for the allyl radical, the calculated values of λ^x_{ij}'s by the INDO method are shown in Table 1. In this case the closed-shell system means the allyl cation.

Inserting Eq. (2) into the Slater-determinants of the RHF (Φ_{RHF}) and UHF methods (Φ_{UHF}), and expanding them by the configuration functions built up from the closed-shell orbitals, we obtain for doublet states^2,

$$\Phi_{\text{RHF}} = \Phi_0 + \sum_i \lambda^R_{im} \Phi_{im} + \sqrt{2} \sum_{i,k} \lambda^R_{ik} \Phi^S_{ik} + \sum_{i,k} (\lambda^R_{ik})^2 \Phi_{\binom{ik}{ik}} + \cdots, \tag{3a}$$

$$\begin{aligned}\Phi_{\text{UHF}} = {} & \Phi_0 + \sum_i \lambda^\beta_{im} \Phi_{im} + \sum_{i,k} \left(\frac{\lambda^\alpha_{ik} + \lambda^\beta_{ik}}{\sqrt{2}}\right) \Phi^S_{ik} + \tfrac{1}{2} \sum_{i,k} \left(\frac{\lambda^\alpha_{ik} + \lambda^\beta_{ik}}{\sqrt{2}}\right)^2 \Phi_{\binom{ik}{ik}} \\ & + \sum_{i,k} \left(\frac{\lambda^\alpha_{ik} - \lambda^\beta_{ik}}{\sqrt{2}}\right) \left(\frac{1}{\sqrt{3}} \Phi^T_{ik} - \sqrt{\tfrac{2}{3}} \Phi^Q_{ik}\right) - \tfrac{1}{2} \sum_{i,k} \left(\frac{\lambda^\alpha_{ik} - \lambda^\beta_{ik}}{\sqrt{2}}\right)^2 \Phi_{\binom{ik}{ik}} + \cdots.\end{aligned} \tag{3b}$$

Then the total energies by the RHF (E_{RHF}) and UHF methods (E_{UHF}) can be expressed as power series in λ using the molecular integrals in terms of closed-

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[1] The coefficient a^α_{im} vanishes since in this case the odd electron is considered to have α-spin.

[2] $\Phi_0 = \|1\bar{1} \ldots i\bar{i} \ldots m\|$, $\Phi_{im} = \|1\bar{1} \ldots i\bar{m} \ldots m\|$, $\Phi^S_{ik} = 1/\sqrt{2}\{\|1\bar{1} \ldots i\bar{k} \ldots m\| - \|1\bar{1} \ldots \bar{i}k \ldots m\|\}$, $\Phi^T_{ik} = 1/\sqrt{6}\{2\|1\bar{1} \ldots ik \ldots \bar{m}\| - \|1\bar{1} \ldots i\bar{k} \ldots m\| - \|1\bar{1} \ldots \bar{i}k \ldots m\|\}$, $\Phi^Q_{ik} = 1/\sqrt{3}\{\|1\bar{1} \ldots ik \ldots \bar{m}\| + \|1\bar{1} \ldots i\bar{k} \ldots m\| + \|1\bar{1} \ldots \bar{i}k \ldots m\|\}$, and $\Phi_{\substack{ik \\ ik}} = \|1\bar{1} \ldots \mathrm{k}\bar{\mathrm{k}} \ldots m\|$.

Table 1. Transformation of open-shell molecular orbitals for allyl radical

	closed-shell molecular orbitals[a]							
	$\langle 1|$	$\langle 3|$	$\langle 4|$	$\langle 8|$	$\langle 11|$	$\langle 13|$	$\langle 15|$	$\langle 16|$
$\{8^R\}$	−0.0121	0.0490	−0.0033	0.9972	0.0196	0.0083	0.0444	−0.0250
$\langle 8^R|$	0.0	0.0	0.0	0.9985	0.0204	0.0097	0.0442	−0.0254
$\{8^\alpha\}$	−0.0101	0.0464	0.0063	0.9975	0.0176	0.0180	0.0375	−0.0277
$\langle 8^\alpha|$	0.0	0.0	0.0	0.9986	0.0183	0.0192	0.0375	−0.0281
$\{8^\beta\}$	−0.0139	0.0504	−0.0008	0.9968	0.0213	−0.0015	0.0513	−0.0225
$\langle 8^\beta|$	0.0	0.0	0.0	0.9982	0.0221	−0.0000	0.0504	−0.0229
	$\langle 2|$	$\langle 5|$	$\langle 7|$	$\langle 12|$	$\langle 14|$	$\langle 17|$		
$\{7^R\}$	0.0064	0.0178	0.9986	−0.0060	0.0474	0.0158		
$\langle 7^R|$	0.0	0.0	0.9987	−0.0057	0.0478	0.0153		
$\{7^\alpha\}$	0.0037	0.0199	0.9991	−0.0094	0.0360	0.0081		
$\langle 7^\alpha|$	0.0	0.0	0.9993	−0.0091	0.0363	0.0078		
$\{7^\beta\}$	0.0093	−0.0169	0.9978	−0.0028	0.0586	0.0230		
$\langle 7^\beta|$	0.0	0.0	0.9980	−0.0023	0.0591	0.0224		

[a] Symmetry; 1, 3, 4, 8, 11, 13, 15, 16 (a_1); 2, 5, 7, 12, 14, 17 (b_1); 6, 10 (b_2); 9 (open MO, a_2)

shell orbitals[3],

$$E_{\mathrm{RHF}}=E_0+\varepsilon_m+2\sum_i \lambda_{im}^R\langle im|mm\rangle+2\sum_{i,k}\lambda_{ik}^R\{2\langle ik|mm\rangle-\langle im|km\rangle\}$$

$$+2\sum_{i,k}(\lambda_{ik}^R)^2(\Delta E_{ik}^S+K_{ik})+\sum_i(\lambda_{im}^R)^2\Delta E_{im}+\cdots, \tag{4a}$$

$$E_{\mathrm{UHF}}=E_0+\varepsilon_m+2\sum_i\lambda_{im}^\beta\langle im|mm\rangle+\sum_i(\lambda_{im}^\beta)^2\Delta E_{im}$$

$$+\sum_{i,k}(\lambda_{ik}^\alpha+\lambda_{ik}^\beta)(2\langle ik|mm\rangle-\langle im|km\rangle)+\tfrac{1}{2}\sum_{i,k}(\lambda_{ik}^\alpha+\lambda_{ik}^\beta)^2(\Delta E_{ik}^S$$

$$+K_{ik})+\sum_{i,k}(\lambda_{ik}^\alpha-\lambda_{ik}^\beta)\langle im|km\rangle+\tfrac{1}{2}\sum_{i,k}(\lambda_{ik}^\alpha-\lambda_{ik}^\beta)^2(\tfrac{1}{3}\Delta E_{ik}^T$$

$$+\tfrac{2}{3}\Delta E_{ik}^Q-K_{ik})+\cdots. \tag{4b}$$

Similar expressions are also obtained for the orbital energies of each method by substituting of Eq. (2) into the Fock-operator F^x.

Using the variational perturbation technique in Eq. (4), the expansion coefficients λ_{ij}^x's are thus connected with each other by the following equations,

$$\lambda_{ik}^\alpha+\lambda_{ik}^\beta=\{-2\langle ik|mm\rangle+\langle im|km\rangle\}/(\Delta E_{ik}^S+K_{ik})$$

$$=2\lambda_{ik}^R, \tag{5a}$$

$$\lambda_{ik}^\alpha-\lambda_{ik}^\beta=-\langle im|km\rangle/(\tfrac{1}{3}\Delta E_{ik}^T+\tfrac{2}{3}\Delta E_{ik}^Q-K_{ik}), \tag{5b}$$

$$\lambda_{im}^\beta=-\langle im|mm\rangle/\Delta E_{im}$$

$$=\lambda_{im}^R. \tag{5c}$$

The calculated results of SCF fully satisfy the relation of Eq. (5a) as shown in Table 2. By using these relations, we can estimate the contributions of the various configurations or the spin polarization effect in the UHF treatment. For the allyl radical, the weight of the quartet state mainly depends on the spin polarization term arisen from the 6–10($\pi\to\pi^*$) transition[4] [3].

We approximate Eq. (4) to second-order in terms of λ, since the terms higher than third-order will be negligibly small (see Table 2) and use the relation of Eq. (5), then,

$$\Delta E_{\mathrm{RHF}}=E_{\mathrm{RHF}}-E_0$$

$$\simeq\varepsilon_m-\tfrac{1}{2}\sum_{i,k}\{2\langle ik|mm\rangle-\langle im|km\rangle\}^2/(\Delta E_{ik}^S+K_{ik})-\sum_i\langle im|mm\rangle^2/\Delta E_{im}$$

$$=\varepsilon_m+E_R, \tag{6a}$$

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[3] $\Delta E_{im}=\varepsilon_m-\varepsilon_i-2J_{im}+J_{mm}+K_{im}$, $\Delta E_{ik}^S=\varepsilon_k-\varepsilon_i-J_{ik}+2K_{ik}-J_{im}+J_{km}+\frac{1}{2}(K_{im}-K_{km})$, $\Delta E_{ik}^T=\Delta E_{ik}^S-2K_{ik}+K_{im}+K_{km}$, and $\Delta E_{ik}^Q=\Delta E_{ik}^S-2K_{ik}-\frac{1}{2}(K_{im}+K_{km})$.

[4] For odd alternant hydrocarbons, a relation of $\langle im|km\rangle>\langle ik|mm\rangle$ always sets up.

Table 2. Expansion coefficients for RHF and UHF molecular orbitals of allyl radical

$i-k$[a]	λ_{ik}^{R}	$\frac{1}{2}(\lambda_{ik}^{\alpha}+\lambda_{ik}^{\beta})$	$\frac{1}{2}(\lambda_{ik}^{\alpha}-\lambda_{ik}^{\beta})$
4–11	0.0196	0.0198	−0.0089
4–13	−0.0269	−0.0265	0.0067
4–15	−0.0105	−0.0105	0.0044
4–16	−0.0172	−0.0171	0.0052
5–12	−0.0216	−0.0217	0.0083
5–14	−0.0177	−0.0180	0.0039
5–17	0.0217	0.0221	−0.0068
6–10	0.0366	0.0362	0.1383
7–12	−0.0057	−0.0057	−0.0034
7–14	0.0478	0.0477	−0.0114
7–17	0.0153	0.0151	−0.0073
8–11	0.0204	0.0202	−0.0019
8–13	0.0097	0.0096	0.0096
8–15	0.0442	0.0440	−0.0065
8–16	−0.0254	−0.0255	−0.0026

[a] See the footnote in Table 1.

Table 3. (a) Calculated values of ionization energy I_p and electron affinity E_A by INDO (ev)

		$-\varepsilon_{\text{closed}}$	ΔE_{RHF}	ΔE_{UHF}	$-\varepsilon_{\text{UHF}}^{x}$	x
NO_2	I_p	12.88	13.05(0.17)[a]	13.15(0.27)	13.38(0.50)	α
	E_A	−1.23	−1.35(0.12)	−1.45(0.22)	−1.71(0.48)	β
Allyl	I_p	8.69	9.27(0.58)	9.66(0.97)	10.61(1.92)	α
	E_A	−0.38	−0.96(0.58)	−1.35(0.97)	−2.31(1.93)	β
CH_3	I_p	11.62	12.34(0.74)	12.38(0.76)	13.13(1.51)	α
C_2H_4	E_A	−5.90	−5.21(0.69)	−5.19(0.71)	−4.49(1.41)	α
H_2CO	E_A	−4.40	−3.89(0.51)	−3.86(0.54)	−3.20(1.20)	α

(b) Calculated values of ionization energy I_P by MINDO/3 (ev)

	$-\varepsilon_{\text{closed}}$	ΔE_{UHF}	$-\varepsilon_{\text{UHF}}^{x}$	x
NO_2	9.47	9.69(0.22)	9.88(0.41)	α
N_2O	11.12	10.67(0.45)	10.23(0.89)	β
H_2CO	10.73	10.38(0.35)	9.99(0.74)	β
H_2CCO	9.16	8.84(0.32)	8.57(0.59)	β
CH_3OH	11.00	10.62(0.38)	10.09(0.81)	β
CH_3CH_3	11.76	11.50(0.26)	11.23(0.53)	β

[a] The numbers in parentheses are the absolute values of the difference between the closed and the corresponding quantity.

[b] The SCF procedures did not converge for CH_3^- anion, $C_2H_4^+$ cation and H_2CO^+ cation radicals.

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\begin{aligned}
\Delta E_{\mathrm{UHF}} &= E_{\mathrm{UHF}} - E_0 \\
&\simeq \varepsilon_m + E_R - \tfrac{1}{2}\sum_{i,k} \langle im|km\rangle^2/(\Delta E^T_{ik} - K_{km} - K_{im} - K_{ik}) \\
&= \varepsilon_m + E_R + E_P. \qquad (6\mathrm{b})
\end{aligned}
$$

Approximate relations for orbital energies are obtained in a similar manner. In the level of the Koopmans' theorem, the electron affinity $-\varepsilon^{\alpha}_{m}$ and the ionization energy $-\varepsilon^{\beta}_{m}$ for neutral molecules are expressed as [5],

$$\varepsilon^{\alpha}_{m},\ \varepsilon^{\beta}_{m} \simeq \varepsilon_m + 2(E_R + E_P), \tag{7}$$

where usually $\varepsilon_m > 0$ for α and $\varepsilon_m < 0$ for β. For radicals, contrary to the case of neutral molecules, $-\varepsilon^{\beta}_{m}(\varepsilon_m < 0)$ and $-\varepsilon^{\alpha}_{m}(\varepsilon_m > 0)$ mean the electron affinity and the ionization energy, respectively. For the orbital energy by the RHF method (ε^{R}_{m}), we cannot give a simple expression, since the second order term in Eq. (8) is not negligibly small. That is,

$$\varepsilon^{R}_{m} - \tfrac{1}{2}J_{mm} = \varepsilon_m + E_R + O(\lambda^2). \tag{8}$$

The concrete expressions to the total energies and the orbital energies for open-shell systems connected with the closed-shell orbitals are now obtained. Table 3 shows the calculated results of these properties for some organic radicals and molecules. The difference between ε^{α}_{m} or ε^{β}_{m} and ε_m is about twice as much

Table 4. Approximate relations between E_{UHF}, E_{AUHF} and E_{SEHF} for higher spin states

$S=1$	B			F		
	ΔE[a]	(I)[b]	(II)[c]	ΔE	(I)	(II)
E_P	0.00025	1.00	1.00	0.00146	1.00	1.00
ΔE_{AUHF}	0.00042	1.68	1.67	0.00247	1.69	1.67
ΔE_{SEHF}	0.00075	3.00	3.00	0.00476	3.29	3.00

$S=2$	C			O		
	ΔE	(I)	(II)	ΔE	(I)	(II)
E_P	0.00137	1.00	1.00	0.00418	1.00	1.00
ΔE_{AUHF}	0.00200	1.46	1.50	0.00601	1.44	1.50
ΔE_{SEHF}	0.00253	1.85	2.00	0.00748	1.79	2.00

$S=3$	N		
	ΔE	(I)	(II)
E_P	0.00361	1.00	1.00
ΔE_{AUHF}	0.00485	1.34	1.40
ΔE_{SEHF}	0.00550	1.52	1.67

[a] Reference [7].

[b] Relative values.

[c] The approximate relation of Eq. (9).

the difference between ΔE_{UHF} and ε_m. This is in good agreement with the result from Eqs. (6b) and (7).

The relation between the various types of the ionization energy and the electron affinity for radicals is written as $|-\varepsilon_m| < |\Delta E_{\mathrm{RHF}}| < |\Delta E_{\mathrm{UHF}}| < |-\varepsilon^\alpha$ or $-\varepsilon^\beta|$, and for molecules as $|-\varepsilon_m| > |\Delta E_{\mathrm{RHF}}| > |\Delta E_{\mathrm{UHF}}| > |-\varepsilon^\beta$ or $-\varepsilon^\alpha|$. That is, the energy relation between the case for radicals and that for molecules reveals a reverse trend as expected from Eq. (7).

In case of higher spin states, Nakatsuji [6] gave a general form of the energy expression for the UHF(E_{UHF}), for after single annihilation (E_{AUHF}), and for the spin-extended HF(E_{SEHF}). Approximating that all the K_{ij} integrals in $\Delta E_{ik}^{\mathrm{s}}$ and $\Delta E_{ik}^{\mathrm{s}+1}$ terms have the same value, we obtain,

$$\Delta E_{\mathrm{AUHF}} \simeq \{(S+4)/(S+2)\} E_P, \tag{9a}$$

$$\Delta E_{\mathrm{SEHF}} \simeq \{(S+2)/S\} E_P, \tag{9b}$$

where we denote the number of unpaired electrons by S. Table 4 shows that these approximate relations are good agreement with the calculated results by Goddard [7] for open-shell atoms.

The present approximation scheme is attractive in view of its simplicity of the analysis of the energy relation between the RHF and UHF methods, and its predictability of the results for the AUHF and SEHF methods.

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5. In Eq. (7), the term $\sum_{ik} [(\lambda_{ik}^{\alpha})^2 + (\lambda_{ik}^{\beta})^2](J_{km} - J_{im})$ for ε_m^α is neglected, since $(J_{km} - J_{im})$ may be negligibly small. The situation is, however, different in the RHF treatment. The term for ε_m^R, $\sum_k (\lambda_{im}^R)^2 (J_{mm} - 2J_{im} + K_{im})$, may be considerably large
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