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Partner Orbitals in Hartree-Fock Theory

Kimihiko Hirao
Department of Chemistry, College of General Education, Nagoya University, Chikusa-ku, Nagoya 464

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The orbital ambiguity in the Hartree-Fock theory is removed in such a way as to improve the convergence property of the configuration interaction calculation. A practical proposal is made to obtain efficient orbitals for use in construction of wavefunctions. These orbitals are called the zeroth-order natural orbitals and their partner orbitals. It is also demonstrated by an illustrative calculation that use of partner orbitals rather than SCF orbitals gives much more rapid convergence and greater physical insight.

The variational condition in the Hartree-Fock (HF) theory determines the occupied and virtual manifolds, but it does not completely determine the individual orbitals belonging to each manifold.[1] This orbital ambiguity yields the possibility of obtaining a new set of orbitals within unitary transformations which may be more effective for the investigation of a particular physical problem than the SCF orbitals. Several attempts[2] were made to exploit this arbitrariness to produce physically meaningful virtual orbitals for some specific purposes. These methods, however, usually resolve the orbital ambiguity according to the criterion that the orbitals should change as little as possible under an excitation of a single electron. These orbitals are suitable to describe the singly excited states but do not help to improve the convergence in the perturbation theory and the configuration interaction (CI) calculation based on the HF equation.

The present discussion differs from these at some points in philosophy. We will consider that the orbital ambiguity should be resolved in such a way that the convergence may be improved in the CI calculation based on the HF equation. The orbitals obtained in such a way should be the zeroth-order approximation to the natural orbitals,[3] since they reduce the number of determinants required for any fixed accuracy in the wavefunction compared with most other techniques for selecting orbitals. Perturbation comparison of HF orbitals and natural orbitals indicates that the coupling of HF occupied and virtual manifolds occurs only in second order due to the Brillouin theorem.[4] This suggests the possibility that we can define zeroth-order natural orbitals by taking advantage of the arbitrariness of the manifolds. In the present study, we will define 2n zeroth-order natural orbitals for 2n-electron systems. The first n natural orbitals are determined by a unitary transformation of the HF manifold.[5] The remaining n natural orbitals are determined by a transformation of the virtual manifold involving pairing of first n zeroth-order natural orbitals with virtual orbitals. The virtual orbitals are, therefore, transformed so that each virtual orbital is largely localized in the same region as its occupied counterpart. There is no resemblance at all between any one of the SCF virtual orbitals and these transformed ones. We call these virtual orbitals as partner orbitals.

The existence of these partner orbitals is predicted in our previous study[6] of the orbital theories with the formalism of the cluster expansion method. The same kind of orbitals as partner orbitals play an important role in constructing wavefunctions of various orbital theories including electron correlation effects. Also the same kind of orbitals appear and help the HF orbitals when the HF state is unstable, that is, when the HF approximation fails to describe the system. However, when the HF solution is stable, as is usually the case, partner orbitals are embedded in the virtual manifold.

We will show how to resolve the orbital ambiguity to obtain the zeroth-order natural orbitals and their partner orbitals. We will also demonstrate that the use of partner orbitals rather than the SCF orbitals gives much more rapid convergence and greater physical insight.

Definition of Partner Orbitals

We consider the case of a determinatal wavefunction of 2n electrons with n doubly occupied orbitals

$$\Phi_0 = \|\phi_1\bar{\phi}_1 \cdots \phi_k\bar{\phi}_k \cdots \phi_n\bar{\phi}_n\| \tag{1}$$

as determined by an SCF calculation. Since we usually obtain these occupied orbitals from some kind of eigenvalue equations which give us more orbitals than needed, we have the so-called virtual orbitals. The virtual orbitals are mere mathematical by-products, so there are an infinitive number of possible choices of the virtual orbitals, the only requiring to be met being that they should be orthogonal to the HF orbitals. For a set of m orbitals (we assume $m \geq 2n$), of which n are occupied, choose pair orbital of the $(m-n)$ virtual orbitals with each of the n occupied orbitals. Then define the Slater determinants Φ_k obtained by exciting a pair of electrons from occupied ϕ_k to its virtual counterpart orbital ϕ_{k^*},

$$\Phi_k = \|\phi_1\bar{\phi}_1 \cdots \phi_{k^*}\bar{\phi}_{k^*} \cdots \phi_n\bar{\phi}_n\|. \tag{2}$$

Throughout the paper, the indices k, l refer to the occupied orbitals, k*, l* to their virtual counterparts, u, v to the remaining virtual orbitals and i, j to general orbitals. Now consider the total wavefunction expressed as a linear combination of these determinants,

$$\Phi = C_0\Phi_0 + \sum_{k=1}^{n} C_k\Phi_k. \tag{3}$$

We assume Φ is normalized to unity. Namely, the configuration expansion coefficients satisfy

$$C_0^2 + \sum_{k=1}^{n} C_k^2 = 1. \tag{4}$$

This expansion is different from the so-called complete MC-SCF (CMC-SCF) expansion of Clementi and

Veillard,[7] in which all possible pair excitations $\psi_k \rightarrow \psi_i$ are included for a finite set. We call this particluar expansion (3) the Selected Paired Excitational (SPE) expansion to distinguish this from other possible paired excitational expansions. The first order reduced density matrix for Φ is written

$$\rho(1|2) = 2\sum_{k=1}^{n}[(1-C_k^2)\psi_k^*(1)\psi_k(2) + C_k^2\psi_{k^*}^*(1)\psi_{k^*}(2)]. \quad (5)$$

These orbitals ψ_k, ψ_{k^*} constitute, therefore, the natural orbitals for Φ. The $(1-C_k^2)$ is the fractional occupation probability for ψ_k and C_k^2 is that for ψ_{k^*}. The configuration expansion coefficients are obtained by solving the conventional CI eigenvalue problem,

$$\boldsymbol{HC} = \boldsymbol{EC} \quad (6)$$

with $\boldsymbol{E}$ the diagonal energy matrix and $\boldsymbol{H}$ defined by the Hamiltonian matrix elements with respect to the SPE configurations.

The idea of the present method is to arrive at equations for the determination of the "best" HF occupied and virtual orbitals to be used in the SPE expansion of the wavefunction. "Best" is used here in the sense that the "best" occupied and virtual orbitals determined by a unitary transformation on each manifold will yield the lowest possible eigenvalue of (6). Thus, we predict that "best" orbitals are presumably close to the first 2n natural orbitals in the space spanned by the m orthonormal basis functions. Thus, we call the "best" occupied orbitals as the first n zeroth-order natural orbitals and the "best" virtual orbitals as partner orbitals to these occupied orbitals. The CI calculation with these "best" orbitals is called the CI with partner orbitals (CIP).

The energy expectation for Φ is given by

$$\begin{aligned} E = E_0 &- 2\sum_k C_k^2(h_{kk} - h_{k^*k^*} + G_{kk} - G_{k^*k^*}) \\ &- 4\sum_{k>l}\sum[C_k^2(G_{kl} - G_{k^*l}) + C_l^2(G_{kl} - G_{kl^*}]) \\ &- 2C_0\sum_k C_k K_{kk^*}, \end{aligned} \quad (7)$$

where E_0 is the HF energy

$$E_0 = 2\sum_k(h_{kk} + G_{kk}) + 4\sum_{k>l}\sum G_{kl}. \quad (8)$$

Here we set

$$G_{ij} = J_{ij} - \frac{1}{2}K_{ij}, \quad (9)$$

where J_{ij} and K_{ij} are the familiar Coulomb and exchange integrals. We use $\sum_k$ to mean summation over the occupied orbitals k and/or the partner orbitals k*. Variation of E with respect to the orbitals, subject to the condition that the occupied and virtual manifolds are kept fixed, gives

$$\langle\psi_k|(1-C_k^2)F_k - (1-C_l^2)F_l|\psi_l\rangle = 0 \quad (10a)$$

$$\langle\psi_{k^*}|C_k^2F_{k^*} - C_l^2F_{l^*}|\psi_{l^*}\rangle = 0 \quad (10b)$$

$$\langle\psi_v|F_{k^*}|\psi_{k^*}\rangle = 0, \quad (10c)$$

where

$$\begin{aligned} F_k &= F_0 + (1-C_k^2)^{-1}[2\sum_{l(\neq k)} C_l^2(G_{l^*} - G_l) + C_0C_kK_{k^*}] \\ F_{k^*} &= F_0 + 2(G_{k^*} - G_k) + C_0C_k^{-1}K_k. \end{aligned} \quad (11)$$

Here the F_0 is the Fock operator

$$F_0 = h + 2\sum_k G_k \quad (12)$$

and

$$G_l = J_l - \frac{1}{2}K_l, \quad (13)$$

where J_i and K_i are the usual Coulomb and exchange operators. The variational conditions (10a), (10b), and (10c) determine the transformations between HF occupied orbitals, between partner orbitals, and between partner and unpaired virtual orbitals, respectively. These conditions can easily be decoupled with the use of projection operators and transformed into a pseudo-eigenvalue problem.[8]

Now let us examine the physical meaning of these variational conditions. For C_0 near unity and the rest close to zero in magnitude, the F_k can be conceptually approximated by Fock operator F_0. Hence the occupied orbitals are, to the first approximation, just the SCF orbitals. From the secular equation in (6), we have

$$E = E_0 - \sum_k (K_{kk^*})^2/(E_k - E) \quad (14)$$

and

$$C_k = -C_0K_{kk^*}/(E_k - E), \quad (15)$$

where E_k are the energies of Φ_k. Now we see C_k are negative. Hence the partner orbital ψ_{k^*} determined by F_{k^*} is bound not only by the nuclear potential in F_0 but also by the very negative exchange potential, $C_0C_k^{-1}K_k$. As a consequence, the partner orbital ψ_{k^*} remains strongly localized in the region of space occupied by its HF counterpart orbital ψ_k. Thus, the partner orbitals have no resemblance to the eigenfunctions of F_0, that is, the SCF virtual orbitals. The general appearance of the partner orbitals can also be understood from the variational theorem. From (14), we see that $\delta E = 0$ corresponds to finding "best" orbitals which maximize

$$\sum_k (K_{kk^*})^2/(E_k - E_0)$$

to first order approximation. This maximum property, especially maximization of $\sum_k (K_{kk^*})^2$ suggests that virtual orbitals should be transformed so that the partner orbitals are as close as possible to their HF occupied counterpart orbitals. Note here that the partner orbitals are not the localized orbitals but symmetry orbitals.

Numerical Examples

As an illustration we shall treat the He and Be atoms and HF molecule in the HF-Roothaan approximation. Optimizing Φ is carried out in a cyclic way varying C_0, C_k in accordance with the CI method and orbitals in accordance with the SCF scheme. The most important practical question is, will an SCF procedure based on (10) converge? At present it is well known that the program based on MC-SCF theory has convergence problems, so we expect that our program will have the same problems. In the present study, the orbital optimization was carried out by a two-by-two rotation technique and it presents no convergence difficulties.[9,10] Good first approximation, especially for the partner orbitals, is necessary to overcome the convergence

Table 1. Wavefunction for He

Basis function[a]	HF	CIP	SPEMC SCF	CMC SCF[b]
1s orbital				
1s(3.3)	0.12059	0.12059	0.14969	0.14505
2s(3.3)	0.01554	0.01554	0.03295	0.03221
4s(3.3)	0.00559	0.00559	0.00770	0.00826
1s(1.433)	0.96446	0.96446	0.87469	0.82599
2s(1.433)	−0.13474	−0.13474	−0.06105	−0.07289
3s(1.433)	0.05943	0.05943	0.03604	0.04408
4s(1.433)	−0.01065	−0.01065	−0.00496	−0.00671
1s*(2s) orbital				
1s(3.3)		−1.2597	−1.2426	−0.87615
2s(3.3)		−0.99455	−0.98522	−0.75327
4s(3.3)		0.15559	0.13957	0.15869
1s(1.433)		2.2981	2.2471	1.0651
2s(1.433)		−0.84574	−0.79441	0.22336
3s(1.433)		0.60263	0.59184	0.19390
4s(1.433)		−0.15903	−0.15425	−0.07708
CI coefficients				
$1s^2$		0.997987	0.997929	0.997799
$1s^2 \to 1s^{*2}(2s^2)$		−0.063415	−0.064318	−0.065666
$1s^2 \to 3s^2$				−0.008846
$1s^2 \to 4s^2$				−0.002370
$1s^2 \to 5s^2$				−0.000651
$1s^2 \to 6s^2$				0.000243
$1s^2 \to 7s^2$				−0.000052

a) Orbital exponents are given in parentheses.
b) Only 1s and 2s orbitals are listed for comparison.

Table 2. Wavefunction for Be

Basis function[a]	HF	CIP	SPEMC SCF	CMC SCF[b]
1s orbital				
1s(5.6858)	0.20816	0.20920	0.21092	0.21104
1s(2.9479)	0.89086	0.90740	0.90449	0.90573
3s(3.6747)	−0.10624	−0.10230	−0.09872	−0.09800
2s(1.3767)	−0.00655	−0.04422	−0.04890	−0.05248
2s(0.8441)	0.00250	−0.06903	−0.07274	−0.07963
2s orbital				
1s(5.6858)	0.02071	−0.00023	−0.00192	−0.00386
1s(2.9479)	0.21003	0.11984	0.11358	0.10494
3s(3.6747)	0.03412	0.04458	0.04392	0.04494
2s(1.3767)	−0.37676	−0.37421	−0.36843	−0.36824
2s(0.8441)	−0.71473	−0.71139	−0.71527	−0.71431
2s*(3s) orbital				
1s(5.6858)		−0.01099	−0.01076	0.01996
1s(2.9479)		−0.14353	−0.12951	0.09332
3s(3.6747)		−0.78212	−0.81523	0.87586
2s(1.3767)		2.9814	3.0081	3.0515
2s(0.8441)		−2.3402	−2.3501	−2.3687
1s*(4s) orbital				
1s(5.6858)		1.8853	1.8646	1.5771
1s(2.9479)		−1.7880	−1.7526	−1.2947
3s(3.6747)		−0.43786	−0.45474	−0.79337
2s(1.3767)		1.0425	1.0200	1.1372
2s(0.8441)		−0.42954	−0.40784	−0.44322
CI coefficients				
$1s^2 2s^2$		0.99871	0.99879	0.99887
$2s^2 \to 2s^{*2}(3s^2)$		−0.04592	−0.04405	−0.04120
$1s^2 \to 1s^{*2}(4s^2)$		−0.02174	−0.02198	−0.02327
$1s^2 \to 5s^2$				−0.00395
$2s^2 \to 3s^2$				−0.00124
$1s^2 \to 4s^2$				−0.00092
$2s^2 \to 5s^2$				−0.00023

a) Orbital exponents are given in parentheses.
b) The 5s orbital is not listed.

problems. The simple initial guess can be found on the structual analogy to the natural orbitals used in the beyond HF theories. We discussed in Appendix how to get initial orbitals.

We first perform ordinary HF-Roothaan calculation on the ground state of He and Be with STO basis functions and then transformed as above. The results can be seen in Tables 1—3 and Figs. 1—3. For He, the HF orbital ϕ_{1s} is kept fixed during the optimization of its partner orbitals ϕ_{1s^*}. The CIP covers 38.4% correlation energy for He and 14.9% for Be. Especially for He the CIP energy is 99.96% of the radial limit (−2.8790 au) and accounts for 93.5% of the radial correlation energy as defined with respect to the HF energy. The CIP results were compared with a more extensive calculations such as SPEMC-SCF (The variation that mixes occupied and virtual orbitals is considered) and CMC-SCF results. The orbital ambiguity provides 93.6 and 95.0% of the energy improvement of the CMC-SCF calculations over the HF values for He and Be, respectively, indicating the effectiveness of the partner orbital transformation. Comparison with the SPEMC-SCF method indicates that the coupling of the HF occupied and virtual manifolds makes little contribution to the energy improvement. Figures 1—3 illustrate radial dependence of each occupied and its partner orbitals for He and Be. These show the localization of each partner orbital in the region where its occupied counterpart is largest. There is no resemblance at all between any one of the SCF virtual orbitals and these partner orbitals. In view of the nodal property, the 2s* orbital of Be corresponds to the 3s Rydberg orbital and the 1s* to the 4s orbital.

We also applied the method to HF molecule. The basis set used here is Dunning's[11] (9s, 5p/4s) GTO set contracted to (4s, 3p/2s) centered on F and H. Experimental equilibrium geometry, $R=1.7328$ au is used in the present calculation of the ground state of HF. In Table 4 and 5 are presented the transformation matrices which take the SCF occupied and virtual orbitals into zeroth-order natural orbitals and their partner orbitals. The effect of zeroth-order transformation in Table 4 is surprizingly large, suggesting that the correct zeroth-order natural orbitals are not the SCF orbitals. Figure 4 shows controur maps for the zeroth-order natural orbitals and the partner orbitals in case of $R=1.7328$ au. These also illustrate that each partner orbital is localized in the region where the occupied counterpart has a high density.

Table 6 is adiabatic potentials by HF, unrestricted HF (UHF) and CIP methods for HF molecule. The HF method is inadequate for the description of the

Table 3. Calculated energies for He and Be[a)]

	He	Be in au
HF	−2.861680	−14.57292
CIP	−2.877866 (38.4)	−14.58702 (14.9)
SPEMC-SCF	−2.877996 (38.5)	−14.58721 (15.1)
CMC-SCF	−2.878972 (41.1)	−14.58776 (15.7)
Experiment[b)]	−2.90378	−14.6674

a) Recovered correlation energies in percent are given in parentheses. b) E. Clementi, *J. Chem. Phys.*, **38**, 2248 (1963).

Table 4. Unitary matrix for obtaining zeroth-order natural orbitals from HF occupied orbitals; HF molecule $R = 1.7328$ au[a)]

i	j				
	1σ	2σ	3σ	1π	$1\bar{\pi}$
1σ	0.99646	−0.08401	−0.00400		
2σ	0.07613	0.88078	0.46737		
3σ	−0.03574	−0.46602	0.88405		
1π				1.0	
$1\bar{\pi}$					1.0

a) The index i refers to HF orbitals, the index j to zeroth-order natural orbitals.

dissociation process since it does not give the correct dissociation limit. The usual SCF procedure of the HF method does not converge at large internuclear separations. In this region, the HF solution becomes unstable and another solution, having lower energy than the HF solution, must exist. The study of the instability problems of the HF solution tells us that the real triplet instability precedes other types of instability and the UHF solution appears when the HF solution is real triplet unstable.[6)] Thus, we can define 2n UHF natural orbitals[12)] when the HF solution is unstable. From the definition of the partner orbitals, these 2n UHF natural orbitals are similar to what we call zeroth-order natural orbitals and their partner orbitals. The determinant using the first n UHF natural orbitals is approximated as the HF determinant. Of course, they will not be identical, but this determinant differs only in second order from the HF determinant. So we employed the space spanned by these first n UHF natural orbitals as the occupied manifold when the HF solution is unstable.

Figure 5 shows the contour maps for the most important 3σ and $3\sigma^*$ orbitals at several H–F bond distances. At infinite distances of H–F bond, the wavefunction can be reduced asymptotically to the form

$$\begin{aligned}\Phi &= (1/\sqrt{2})\|\cdots(3\sigma\overline{3\sigma}-3\sigma^*\overline{3\sigma}^*)\cdots\| \\ &= \|\cdots(3\sigma+3\sigma^*)/\sqrt{2}\cdot(3\sigma-3\sigma^*)/\sqrt{2}\cdot(\alpha\beta-\beta\alpha)/\sqrt{2}\cdots\|\end{aligned} \tag{16}$$

Figure 5 illustrates $(3\sigma\pm3\sigma^*)/\sqrt{2}$ orbitals at large nuclear separations converge to 1s orbital of H and 2p orbital of F, respectively. Thus, the dissociation process of the H–F bond was reproduced by the present method as most chemists had assumed.

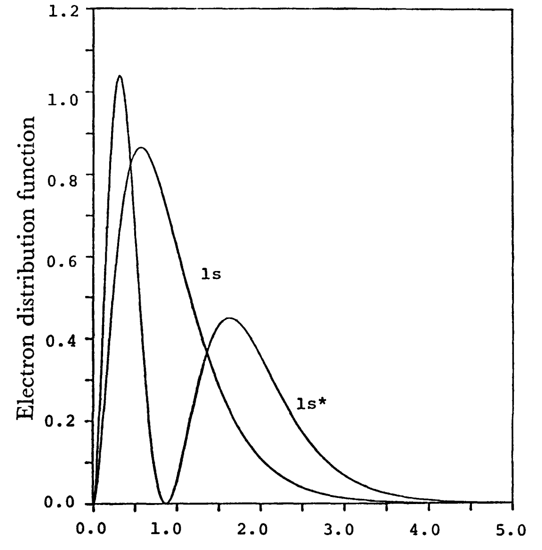


Fig. 1. Radial dependence of the ls and ls* orbitals of He.

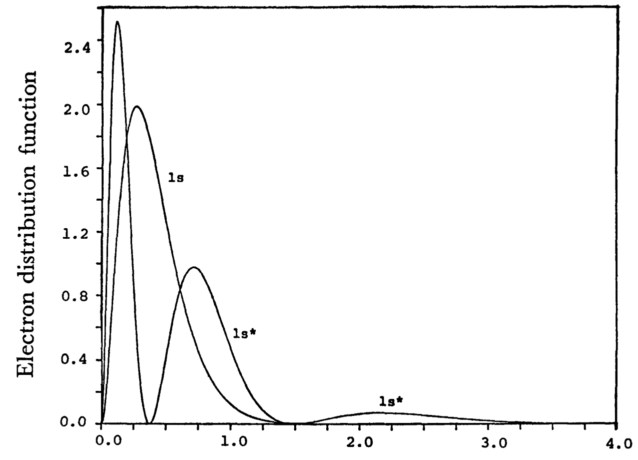


Fig. 2. Radial dependence of the ls and ls* orbitals of Be.

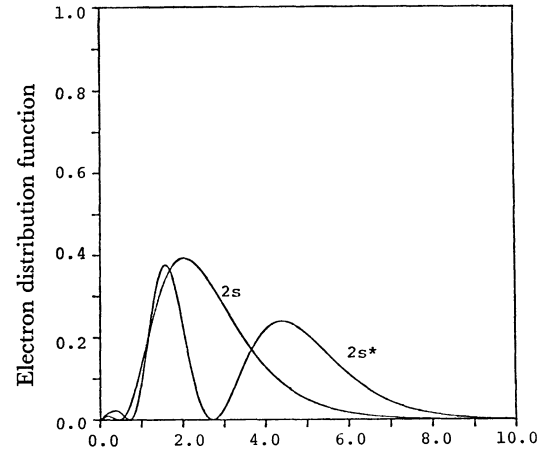
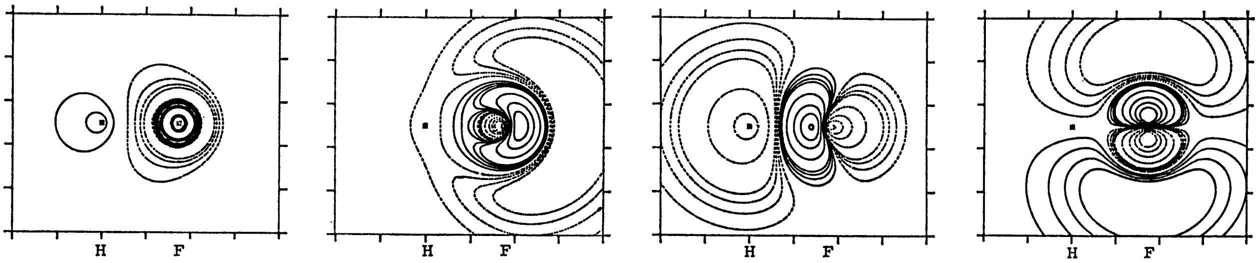


Fig. 3. Radial dependence of the 2s and 2s* orbitals of Be.

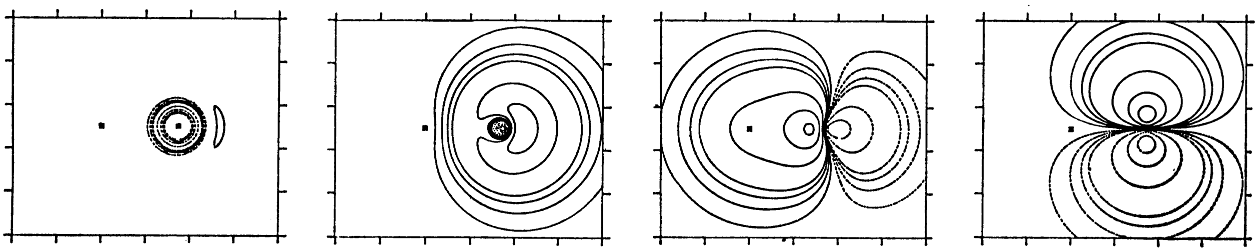
Table 5. Unitary matrix for obtaining partner orbitals from HF virtual orbitals; HF molecule R=1.7328 au[a)]

i	j				
	$1\sigma^*$	$2\sigma^*$	$3\sigma^*$	$1\pi^*$	$1\bar{\pi}^*$
4σ	0.05607	−0.23052	−0.58540		
5σ	0.01585	0.08438	−0.75117		
6σ	0.06465	−0.65456	0.22430		
7σ	0.14818	0.66139	0.16474		
8σ	−0.05127	0.27000	−0.12487		
9σ	−0.98379	0.03075	0.00059		
2π				0.92666	
3π				−0.37589	
$2\bar{\pi}$					0.92666
$3\bar{\pi}$					−0.37589

a) The index i referers to HF virtual orbitals, the index j to partner orbitals.



1σ* orbital 2σ* orbital 3σ* orbital 1π* orbital

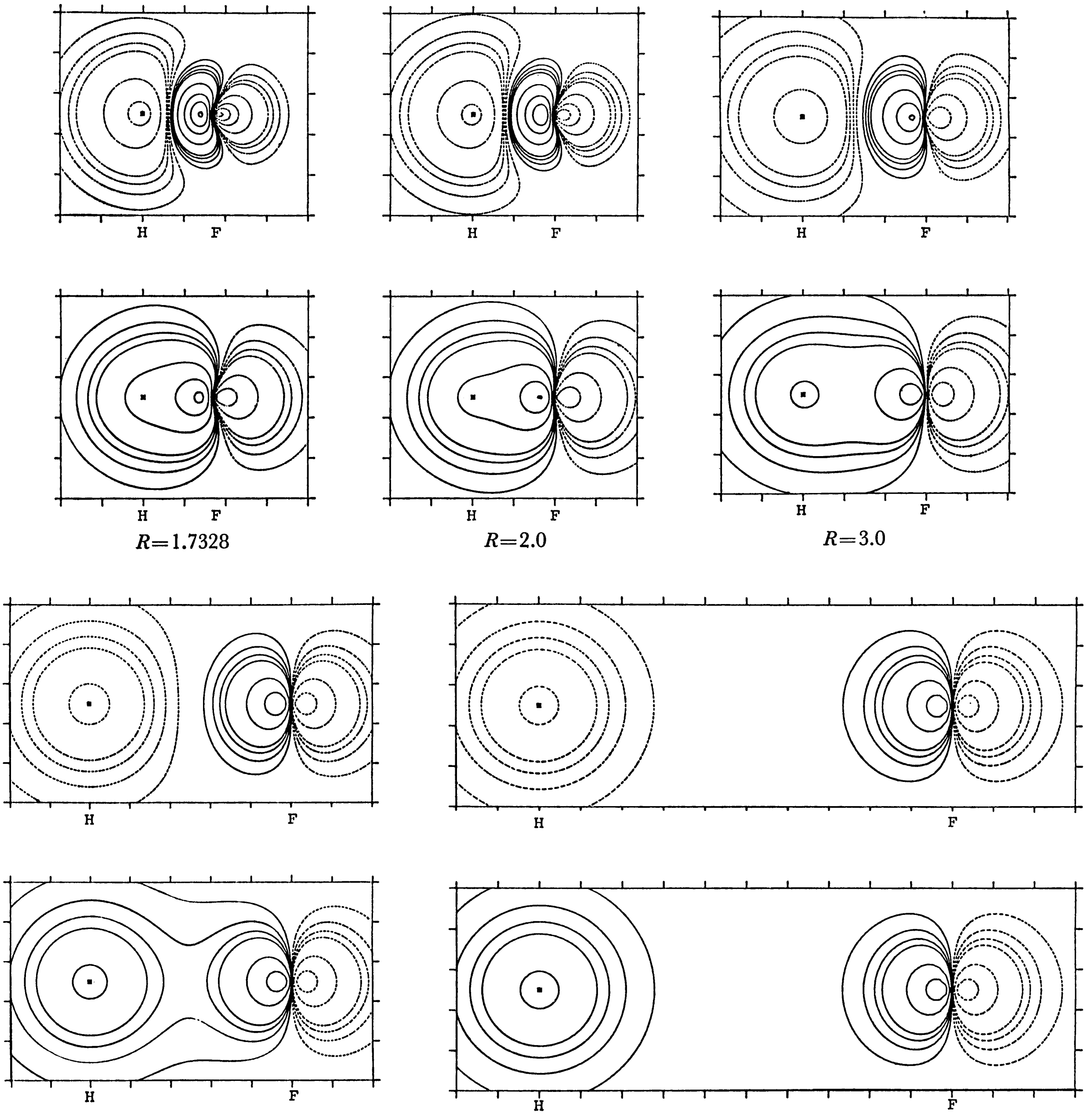


1σ orbital 2σ orbital 3σ orbital 1π orbital

Fig. 4. Contour maps for zeroth-order natural orbitals and their partner orbitals of HF molecule; R=1.7328 au.

Table 6. Energies of HF molecule at several bond distances

	H–F bond distances in au				
	1.7328	2.0	3.0	5.0	10.0
Energy in au					
HF	−100.01795	−100.00460	−99.87084	−99.64488	−99.55020
UHF	—	—	−99.90784	−99.89457	−99.89434
CIP	−100.07912	−100.07219	−99.97815	−99.91576	−99.91063
CI coefficients					
$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2 1\bar{\pi}^2$	0.99116	0.98756	0.94385	0.78358	0.72401
$1\sigma^2 \rightarrow 1\sigma^{*2}$	−0.00827	−0.00840	−0.00841	−0.00723	−0.00667
$2\sigma^2 \rightarrow 2\sigma^{*2}$	−0.02548	−0.02064	−0.01021	−0.00473	−0.00432
$3\sigma^2 \rightarrow 3\sigma^{*2}$	−0.10137	−0.13264	−0.32173	−0.61862	−0.68786
$1\pi^2 \rightarrow 1\pi^{*2}$	−0.05750	−0.05757	−0.05221	−0.04020	−0.03605
$1\bar{\pi}^2 \rightarrow 1\bar{\pi}^{*2}$	−0.05750	−0.05757	−0.05221	−0.04020	−0.03605



R=1.7328 R=2.0 R=3.0

R=5.0 R=10.0

Fig. 5. Contour maps for the 3σ and $3\sigma^*$ orbitals of HF at several distances of H–F bond.

Summary

By taking advantage of the orbital ambiguity of the HF theory, we define the zeroth-order natural orbitals and their partner orbitals. The set of HF natural orbitals which is easy to construct, is fairly good enough to give the desired accuracy and facilitates physical interpretation of the results.

The CI with partner orbitals accounts for only intrapair correlation effect of the electron correlation. A theory can be developed which involves interpair correlation effect as well as intrapair correlation, if we choose an approximate CI expansion in (3) instead of the SPE expansion. In such a theory, however, the simplicity and ease of interpretation found in the present theory may be no longer preserved.

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Appendix (How to Get the Initial Orbitals)

The initial orthonormal orbitals are generated by the corresponding orbital transformation procedure.

Let $\hat{a}_k$ and $\hat{b}_k$ be an approximated solution and its correction to the HF solution, respectively. Then the HF natural orbitals $\hat{c}_k$ and partner orbitals $\hat{c}_k{}^*$ are expressed in the form[6]

$$\hat{c}_k = (\hat{a}_k + \xi_k \hat{b}_k)/(1+\xi_k{}^2)^{1/2}$$

$$\hat{c}_{k*} = (\hat{b}_k - \xi_k \hat{a}_k)/(1+\xi_k{}^2)^{1/2}$$

where the $\hat{a}_k$ and $\hat{b}_k$ are orthonormal and ξ_k are real coefficients.

Assume that the HF solution c_k is known and we have its approximate solution a_k. Given any two sets of orbitals c_k and a_k, there exist equivalent sets $\hat{c}_k$ and $\hat{a}_k$ such that their overlap matrix is diagonal $\langle \hat{c}_{kl} | \hat{a}_l \rangle = \delta_{kl} T_k$ through the so-called corresponding orbital transformation. Then, we can construct $\hat{c}_{k*}$ using the above relations. The problem is the choice of the approximate HF solution sicne the resultant resultant $\hat{c}_k$ and $\hat{c}_{k*}$ depend on the approximate solution employed. In the practical application, we used the approximate solution generated by diagonalizing the core matrix. The method is simple and relatively accurate.

When the HF solution is unstable, the UHF natural orbitals are, of course, good initial orbitals to the partner orbitals.

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