COMMENTS ON THE USE OF UNRESTRICTED HARTREE-FOCK THEORY IN ORBITAL ENERGY CROSSING*

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Curve crossing in a simple two-electron two-orbital model is considered. It is shown that the spin density wave (SDW) solution has the correct crossing points and is closest to the exact solution of all single determinants.

Recently, in an interesting paper [1], Pople considers a two-electron two-orbital model in which there is curve crossing of a singlet and a triplet state. Ordinary molecular orbital theory, using restricted Hartree-Fock (RHF) single-determinantal wavefunctions, predicts a discontinuous change at the point where the energies of the s's' and s"s" singlets cross. As noted by Pople, this is an artifact due to the limited form of the wavefunction which can be circumvented by a CI calculation. Pople considers a single-determinantal wavefunction with complex molecular orbitals which he maintains is the best single-determinantal wavefunction for this model system. However, we have found that the best unrestricted Hartree-Fock (UHF) wavefunction for this system is the SDW [2] wavefunction. The SDW wavefunction, unlike Pople's complex wavefunction, gives the correct singlet-triplet crossings. Furthermore the projected SDW is a very good approximation to the CI result, while the projected complex wavefunction departs considerably from the CI result.

Falicov and Harris [2] have considered the spin density wave (SDW) and charge density wave (CDW) solutions for the two-electron homopolar molecule. Their model is the same as that of Pople except they neglect the atomic exchange and hybrid integrals. However, these integrals are of the utmost importance in the application of UHF theory to the curve crossing problem. In fact if the exchange terms are neglected Pople's solution becomes the MO solution.

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Using the notation of Pople, we considerer the two molecular orbitals $\psi_{s'}$ and $\psi_{s''}$. From the symmetry MO's we construct two localized, orthogonal orbitals:

$$\phi_1 = 2^{-1/2} \left(\psi_{\mathbf{s}'_1} + \psi_{\mathbf{s}''_1} \right), \tag{1}$$

$$\phi_2 = 2^{-1/2} \left(\psi_{s'} - \psi_{s''} \right). \tag{2}$$

The hamiltonian is given by

$$H = H_1 + H_2 + 1/r_{12}, \tag{3}$$

where H_i contains the interactions of electron *i* with the nuclei and with the core electrons. As mentioned by Pople, the nuclear motions giving rise to the curve crossing will also modify the core energy, and in a complete treatment this change in the core energy should also be included. We further define

$$\langle 1|H|1\rangle = \langle 2|H|2\rangle = \alpha, \tag{4}$$

$$\langle 1|H|2\rangle = \beta, \tag{5}$$

where the single-particle diagonal term is set equal to zero for convenience and β corresponds to the singleparticle off-diagonal term. ($\beta < 0$ if ψ_s , has a lower oneelectron energy than $\psi_{s''}$.)

Following Pople, we now consider the two-electron integrals in terms of the equivalent orbitals:

$$(\mu\nu\lambda\delta) = \iint \phi_{\mu}(1)\phi_{\nu}(1)(1/r_{12})\phi_{\lambda}(2)\phi_{\delta}(2), \qquad (6)$$

$$\beta' = \beta + (11|12), \tag{7}$$

$$A = (11|11) - (11|22) \tag{8}$$

$$K_{\rm ex} = (12|12).$$
 (9)

For physically meaningful values of the parameters, Δ and $K_{ex} > 0$. We will not consider the case $\Delta < 0$ which has been considered by Falicov and Harris. We will also maintain Pople's assumption that $\Delta > 2K_{ex}$ (this is true whenever ϕ_1 and ϕ_2 are more localized than ψ_s , and $\psi_{s''}$). Table 1 gives the matrix elements of the effective hamiltonian H' = H - (11|22).

The molecular orbital solutions are

$${}^{1}\Psi_{s's'} = 2^{-1/2} \psi_{s'}(1) \psi_{s'}(2) [\alpha\beta - \beta\alpha], \qquad (10)$$

$${}^{1}\Psi_{s''s''} = 2^{-1/2} \psi_{s''}(1) \psi_{s''}(2) \left[\alpha\beta - \beta\alpha\right], \tag{11}$$

$$^{1}\Psi_{s's''}$$

$$= \frac{1}{2} \left[\psi_{s'}(1) \psi_{s''}(2) + \psi_{s''}(1) \psi_{s'}(2) \right] \left[\alpha \beta - \beta \alpha \right], (12)$$

 ${}^3\Psi_{s's''}$

$$=\frac{1}{2} \left[\psi_{s'}(1) \psi_{s''}(2) - \psi_{s''}(1) \psi_{s'}(2) \right] \left[\alpha \beta + \beta \alpha \right], \ (13)$$

with energies

$$\langle {}^{1}\Psi_{\rm s's'} | H | {}^{1}\Psi_{\rm s's'} \rangle = 2\beta' + \frac{1}{2}\Delta + K_{\rm ex},$$
 (14)

$$\langle {}^{1}\Psi_{{}_{\mathsf{S}''\mathsf{S}''}} | H | {}^{1}\Psi_{{}_{\mathsf{S}''\mathsf{S}''}} \rangle = 2\beta' + \frac{1}{2}\Delta + K_{\mathrm{ex}}, \tag{15}$$

Table 1 The matrix elements of the effective hamiltonian H' = H - (11122), where $|i\uparrow j\downarrow\rangle = 2^{-1/2} (\phi_i \alpha \phi_j - \phi_j \phi_i \alpha)$

	1 †1↓>	2†2↓>	11†21)	12†1↓>
(1†14)	Δ	Kex	β'	β'
12†24>	Kex	Δ	β'	β'
11124>	β'	β'	0	Kex
12†14>	β'	β'	Kex	0

$$\langle {}^{1}\Psi_{\mathsf{s}'\mathsf{s}''}|H|\,{}^{1}\Psi_{\mathsf{s}'\mathsf{s}''}\rangle = \Delta - K_{\mathsf{ex}},\tag{16}$$

$$\langle {}^{3}\Psi_{s's''} | H | {}^{3}\Psi_{s's''} \rangle = -K_{ex}.$$
 (17)

The only off-diagonal matrix element in this representation is

$$\langle {}^{1}\Psi_{S'S'} |H| {}^{1}\Psi_{S''S''} \rangle = \frac{1}{2} \Delta,$$
 (18)

so that the CI energies for the two mixed singlets are

$$E(\text{CI}) = \frac{1}{2} \Delta + K_{\text{ex}} \pm \frac{1}{2} [\Delta^2 + 16(\beta')^2]^{1/2}.$$
 (19)

The general UHF ground-state wavefunction is a Slater determinant of the form [2]:

$$|(\cos\theta_{1}\phi_{1} + e^{i\chi_{1}}\sin\theta_{1}\phi_{2})\alpha \times (\cos\theta_{2}\phi_{1} + e^{i\chi_{1}}\sin\theta_{2}\phi_{2})\beta\rangle, \qquad (20)$$

where $\theta_1, \theta_2, \chi_1$ and χ_2 are variationally determined in order to minimize the energy: $E^1 = \langle H^1 \rangle$.

Table 2 gives the results of the variational calculation. In the localized orbital representation the wavefunctions are:

$$|\text{SDW1}\rangle = |(\cos\theta \ \phi_1 + \sin\theta \ \phi_2) \alpha |$$

$$\times (\sin\theta \ \phi_1 + \cos\theta \ \phi_2) \beta\rangle, \qquad (21)$$

Table 2

UHF solution	Value of parameters					Range over which UHF solution is
	x1	X2	θ1	02	parameter	than RHF solution
SDW1	0	π	θ	θ-π	$\sin 2\theta = -2\beta'/(\Delta + 2K_{ex})$	$ 2\beta' \leq \Delta + 2K_{\text{ex}}$
CDW1	0	0	θ	θ	$\sin 2\theta = \frac{2\beta'}{(\Delta - 2K_{\rm ex})}$	$ 2\beta' \leq \Delta - 2K_{\rm ex}$
CSDW1		µ	$\pi/4$	π/4	$\cos \mu = -\beta'/K_{ex}$	$ \mathcal{G}' < K_{ex}$
CCDW1	μ	μ	π/4	π/4	$\cos \mu = -\beta' / K_{\text{ex}}$	$ \mathcal{G}' < K_{ex}$

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$\times (\cos\theta \phi_1 + \sin\theta \phi_2)\beta\rangle,$	(22)
$CDW1\rangle = I(\cos\theta \phi_1 + \sin\theta \phi_2) \alpha$	
$\times (\cos\theta \phi_1 + \sin\theta \phi_2) \beta \rangle,$	(23)

$$|CDW2\rangle = |(\sin\theta \phi_1 + \cos\theta \phi_2) \alpha|$$

 $|SDW2\rangle = I(\sin\theta \phi_1 + \cos\theta \phi_2) \alpha$

 $\times (\sin\theta \,\phi_1 + \cos\theta \,\phi_2)\beta\rangle, \tag{24}$

$$|CSDW1\rangle = \frac{1}{2} |(\phi_1 + e^{ju}\phi_2)\alpha(\phi_1 + e^{-ju}\phi_2)\beta\rangle,$$
 (25)

$$|\text{CSDW2}\rangle = \frac{1}{2} |(\phi_1 + e^{-iu}\phi_2)\alpha(\phi_1 + e^{iu}\phi_2)\beta\rangle.$$
 (26)

Pople's solutions are:

 $|\text{CCDW1}\rangle = \frac{1}{2} |(\phi_1 + e^{iu}\phi_2)\alpha(\phi_1 + e^{iu}\phi_2)\beta\rangle, \quad (27)$

$$|\text{CCDW}_2\rangle = \frac{1}{2} |(\phi_1 + e^{-iu}\phi_2) \alpha (\phi_1 + e^{-iu}\phi_2) \beta\rangle.$$
(28)

There exist two UHF solutions of each type and these have the same energy in each case. We can take the appropriate linear combination of the two degenerate solutions and get a solution of restored symmetry. The SDW solutions violate spin symmetry, that is, they are not eigenfunctions of S^2 . Forming the linear combination $|SDW1\rangle + |SDW2\rangle$ is equivalent to projecting the singlet spin function out of $|SDW1\rangle$ or $|SDW2\rangle$. Similarly we can eliminate the singly excited singlet contaminant from the CDW solutions and obtain a further lowering of the energy. In the CCDW and CSDW this symmetrization is equivalent to projecting out the real part of the complex wavefunction.

It is illuminating to consider the UHF solutions in the representation of the symmetry-type molecular orbitals:

$$|\text{SDW}\rangle \approx s's' - \lambda^2 s''s'' + \lambda (s's'' - s''s'), \qquad (29)$$

$$|CDW\rangle \approx s's' + \lambda^2 s''s'' + \lambda(s's'' + s''s'),$$
 (30)

 $|\text{CSDW}\rangle \approx s's' + \lambda^2 s''s'' + i\lambda(s's'' - s''s'),$ (31)

 $|CCDW\rangle \approx s's' - \lambda^2 s''s'' + i\lambda(s's'' + s''s').$ (32)

These four cases, in somewhat different context, have

	Table 3
UHF solution	Energy (H')
SDW	$\frac{-2(\beta')^2}{\Delta+2K_{\rm eX}}$
Proj SDW	$\frac{(\Delta+2K_{\text{ex}})^2}{4(\beta')^2+(\Delta+2K_{\text{ex}})^2} \left[K_{\text{ex}} + \frac{4(\beta')^2(\Delta+K_{\text{ex}})}{(\Delta+2K_{\text{ex}})^2} - \frac{8(\beta')^2}{(\Delta+2K_{\text{ex}})} \right]$
CDW	$\Delta + \frac{2(\beta')^2}{\Delta - 2K_{\rm ex}}$
Proj CDW	$\frac{(\Delta - 2K_{\text{ex}})^2}{4(\beta')^2 + (\Delta - 2K_{\text{ex}})^2} \left[\Delta + \tilde{K}_{\text{ex}} + \frac{4(\beta')^2 K_{\text{ex}}}{(\Delta - 2K_{\text{ex}})^2} + \frac{8(\beta')^2}{(\Delta - 2K_{\text{ex}})} \right]$
CCDW	$\frac{\Delta}{2} - \frac{\left(\beta'\right)^2}{K_{\rm ex}}$
Proj CCDW	$\frac{(\beta')^{2} \Delta - 3(\beta')^{2} K_{ex} + K_{ex}^{3}}{(\beta')^{2} + K_{ex}^{2}}$
CSDW	$\frac{\Delta}{2} - \frac{\left(\mathcal{G}'\right)^2}{K_{ex}}$
Proj CSDW	$\frac{\Delta K_{ex}^2 - 3(\beta')^2 K_{ex} + K_{ex}^3}{(\beta')^2 + K_{ex}^2}$

been discussed by Paldus and Čížek [3] and also by Musher [4]. The two complex UHF solutions give the same energy. However the projected solutions differ in energy, the projected CCDW being of lower energy and giving a better description of the curve crossing.

In treating the curve crossing using projected SDW or projected CSDW we are not projecting out the iowest energy component but rather the ¹S component (that comprised of ${}^{1}\psi_{s's'}$ and ${}^{1}\psi_{s's''}$). Clearly, in the region of interest, the triplet component is of lowest energy. Also it should be made clear that by projected UHF we mean projection after variation. If we reverse these two operations, we reproduce the CI results. This is due to the simplicity of the model under consideration; in general, projection prior to variation leads to an alternant MO type of function.

The final results for the energies are given in table 3. Examination of the table leads to the conclusion that the CDW and projected CDW solutions are not of

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Fig. 1. The energies of the various approximations versus β' . The configuration interaction (exact) energies are dotted lines; the approximate energies are full lines.

much interest when $\Delta > 2K_{ex}$. We also see that, for the range of their definition $(|\beta'| < K_{ex})$, the projected CCDW is of lower energy than the projected CSDW solution. Comparison of E_{SDW} and E_{CCDW} yields the important result that $E_{SDW} < E_{CCDW}$ for $|\beta'| < K_{ex}$.

In fig. 1 the various energies are plotted as a function of β^{t} . Following Pople, we neglect the variation in Δ , K_{ex} , (11122) and the core energy and consider

Table	4
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Point	Value of β'	Value of energy (E')	Intersecting curves	
P"	$[K_{\text{ex}}(K_{\text{ex}}+\frac{1}{2}\Delta)]^{1/2}$	-K _{ex}	³ A, SDW, pioj.	
Q"	$K_{\rm ex} + \frac{1}{4} \Delta$	-Kex	³ A, MO	
$\mathbf{L}^{\vec{n}}$.	$K_{\text{ex}} + \frac{1}{2}\Delta$	$-\frac{1}{2}\Delta - K_{\text{ex}}$	MO, SDW,	
R"	K _{ex}	$\frac{1}{2}\Delta - K_{\text{EX}}$	MO, CCDW proj CCDW	
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only variation of β' . The totally symmetric singlet states are denoted by ¹S, and the non-totally symmetric states by ¹A and ³A.

The points of intersection of the various curves are given in table 4. The change from the configuration $...(s')^2$ to $...(s'')^2$ occurs in a continuous manner in both the SDW and CCDW approaches. The SDW description is preferable due to its greater range of validity. The SDW gives the correct singlet-triplet intersections, whereas the CCDW solution is not even defined in the region of the intersection (therefore the singlettriplet intersection obtained in Pople's approach is the MO intersection)^{*}. We also found that the projected SDW solution is a much better approximation to the CI result than is the projected CCDW solution.

In conclusion, we have shown for the simple model considered that the best singly determinantal wavefunction is an SDW, rather than the complex wavefunction of Pople. It would be most interesting to study the use of UHF theory in more complicated curve crossing situations. We believe, based on the papers of Čížek and Paldus [3] and of other investigators[†], that in general the SDW approach will better describe the curve corssing than will a complex molecular orbital approach.

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- * If we extend the region of definition of E_{CDW} (this is not really valid since it is equivalent to saying $|\cos \mu| > 1$) we find that E_{CCDW} and E_{3A} intersect at P',P". This is probably a fortuitous occurrence. In any case, if we try a similar extension in the projected CCDW, we still get the incorrect intersection.
- † An interesting paper by Fukutome [5] on the use of UHF theory of chemical reactions appeared after we completed the calculations discussed in this paper. Fukutome uses UHF theory to analyze the rotation about the double bond in ethylene and also considers the face to face addition of the two ethylenes. He suggests the possibility of a connection between the occurrence of UHF solutions of broken symmetry and the rules of Woodward and Hoffmann.

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