

EXCITED STATES OF H₂O USING IMPROVED VIRTUAL ORBITALS ‡

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A technique for solving the Hartree-Fock equations is proposed which has the property that the virtual orbitals from the ground state wavefunction are variationally correct approximations to the self-consistent orbitals for the excited states. This allows a whole series of excited state wavefunctions to be obtained from one calculation. This method was applied to a number of low-lying singlet and triplet excited states of H₂O, and found to lead to good results.

1. INTRODUCTION

In the Hartree-Fock approximation the ground state wavefunction for a system such as H₂O is expressed as a Slater determinant involving a number of doubly occupied orbitals [1]. In many cases it should be possible to obtain an adequate description of a low-lying excited state of the molecule by simply replacing one of the ground state orbitals in the determinant by an excited state orbital [2]. For example, for the lowest ¹B₁ - ¹A₁ transition of H₂O we would replace the 1b₁ orbital with a 4a₁ orbital. It has often been suggested that the virtual (unoccupied) orbitals from ground state calculations would form suitable excited state orbitals (e.g., see ref. [2] pp 79-80). However, it has also been noted (for example, see ref. [3]) that the virtual orbitals usually have positive eigenvalues while the actual excited state orbital usually should be bound. It has been observed that this behavior is caused by the presence of the so-called self Coulomb and exchange operators in the usual Hartree-Fock Hamiltonian [4]. These self terms produce virtual orbitals of an *N* electron system appropriate for an *N* + 1 electron system. Thus the virtual orbitals of a neutral molecule often have positive energies (i.e., are unbound).

We note here that the self terms are artificially introduced into the HF equations for computational convenience and that if they are deleted

the new virtual orbitals see a correct field and form variationally correct approximation to the excited state orbitals.

We have applied this approach to a number of excited states of H₂O and find results far improved over those from the usual method. In particular many of these improved virtual orbitals have negative eigenvalues corresponding to the ionization potentials of the excited states.

2. VIRTUAL ORBITALS AND THE VARIATIONAL EQUATIONS

Consider a Slater determinant

$$a(\psi_1\psi_2\dots\psi_N) \quad (1)$$

composed of spin orbitals ψ_i . The energy of this is

$$\langle \mathcal{H} \rangle = \sum_i^N \langle \psi_i | h | \psi_i \rangle + \sum_{i>j} (J_{ij} - K_{ij}), \quad (2)$$

where *h* contains the one-electron operators (kinetic energy and nuclear attraction) and *J_{ij}* and *K_{ij}* are the usual Coulomb and exchange integrals between spin orbitals ψ_i and ψ_j . By requiring the energy to be stationary under variation of the orbital ψ_i , we find that each optimum ψ_i is a solution of

$$H_i\psi_i = \epsilon_i\psi_i, \quad (3)$$

where

$$H_i = h + \sum_{j \neq i}^N (J_j - K_j)$$

and *J_j* and *K_j* are the usual Coulomb and exchange

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operators (including spin) [2]. Each H_i has a set of eigenfunctions from which we select just one solution to be occupied in (1); the other solutions of H_i are called virtual orbitals.

Now consider the Hamiltonian

$$H^{\text{HF}} \equiv h + \sum_j^N (J_j - K_j) . \quad (4)$$

Since $(J_j - K_j)\psi_i = 0$, we have $H^{\text{HF}}\psi_i = H_i\psi_i$, and the occupied orbitals are all eigenfunctions of H^{HF} ,

$$H^{\text{HF}}\psi_i = \epsilon_i\psi_i . \quad (5)$$

Since (5) requires construction of only one operator rather than N operators as in (3), (5) is usually (e.g., see ref. [2] p. 73) employed in solving for the self-consistent orbitals of (1).

Now consider a wavefunction in which one spin orbital, ψ_i , in the determinant (1) is replaced by a new orbital ψ_l and the other orbitals are unchanged

$$\alpha\psi_1 \dots \psi_{i-1}\psi_l\psi_{i+1} \dots \psi_N . \quad (1')$$

If we require the energy of (1') to be stationary under variation of ψ_l , we obtain the equation $H_i\psi_l = \epsilon_l\psi_l$, where H_i is exactly the same as the operator for ψ_i in (3). That is, the variationally correct orbital, ψ_l , for (1') is a virtual orbital of H_i from the ground state calculation. Thus to the extent to which it is a good approximation to assume that the remaining orbitals do not change upon excitation of ψ_i to ψ_l , the set of virtual solutions of H_i comprises all such singly excited states of the molecule. Note here that the orbital energy ϵ_l is the negative of the ionization potential of (1'), in this same approximation that the other orbitals remain frozen; that is

$$\epsilon_l = \langle \psi_l | h | \psi_l \rangle + \sum_{j \neq i, l} (J_{jl} - K_{jl}) .$$

However, because of the self-terms in H^{HF} , the variationally determined excited state orbital, ψ_l , is *not* a virtual solution of H^{HF} . Consequently we should not expect the virtual orbitals of H^{HF} to approximate excited state orbitals. Indeed if we consider the $N+1$ electron wavefunction $a(\psi_1 \dots \psi_N \psi_l')$, where $\psi_1 \dots \psi_N$ are forced to be the orbitals from (1), then the variational equation for the optimum ψ_l' is just $H^{\text{HF}}\psi_l' = \epsilon_l\psi_l'$, where H^{HF} is given by (5). Thus the virtual orbitals of H^{HF} are appropriate for excited states of the $N+1$ electron system. If the N electron system is a neutral molecule, then the virtual orbitals of H^{HF} are suitable for the nega-

tive ion and not for the excited states of the molecule. In fact, the eigenvalues of these virtual orbitals are usually all positive [3].

We now express ψ_i as a product of a spatial orbital, ϕ_i , and a spin function, $\sigma_i = \alpha$ or β . For molecules such as H_2O the ground state wavefunction (1) contains each ϕ_i twice. In this case the optimum orbital ϕ_l for the excited state Slater determinant (1') is a solution of

$$\begin{aligned} H_i^{\text{EX}}\phi_l &= \left[h + \sum_{j \neq i}^{N/2} (2\mathcal{J}_j - \mathcal{K}_j) + \mathcal{J}_i \right] \phi_l \\ &= \epsilon_l\phi_l + \sum_{j \neq l}^{N/2} \epsilon_{jl}\phi_j , \end{aligned} \quad (6)$$

where orbital ϕ_i is singly occupied in the excited state wavefunction (1') and the spin projection is taken as $\mathcal{M}_S = 0$. (If $\mathcal{M}_S = 1$, \mathcal{J}_i is replaced by $\mathcal{J}_i - \mathcal{K}_i$.) Here \mathcal{J}_j and \mathcal{K}_j are defined over spatial orbitals and coordinates (the spin coordinates have been integrated over) [2]. The off-diagonal Lagrange multipliers, ϵ_{jl} , ensure that ϕ_l is orthogonal to the other orbitals occupied in (1').

In terms of a finite set of basis functions, $\{\chi_\mu\}$, orthogonal to the occupied orbitals of (1), we obtain the usual matrix Hartree-Fock equations ‡

$$\sum_\nu H_{\mu\nu}^{\text{EX}} C_{\nu l} = \sum_\nu S_{\mu\nu} C_{\nu l} \epsilon_{ll} , \quad (7)$$

where

$$H_{\mu\nu}^{\text{EX}} = \langle \chi_\mu | H_i^{\text{EX}} | \chi_\nu \rangle .$$

For the excited singlet and triplet states ($\mathcal{M}_S = 0$) we replace $\phi_i\alpha\phi_l\beta$ in (1') by $(\phi_i\phi_l \pm \phi_l\phi_i)\alpha\beta$ to obtain the correct spin symmetry (the positive sign is for the singlet and the negative sign is for the triplet). In this case (6) is replaced by

$$H_i^{\text{EX}} = h + \sum_{j \neq i} (2\mathcal{J}_j - \mathcal{K}_j) + \mathcal{J}_i \pm \mathcal{K}_i .$$

We will call the solutions of H_i^{EX} the improved virtual orbitals (IVO), and we denote the virtual orbitals of H^{HF} as the regular virtual orbitals (RVO).

‡ The ϵ_{ij} terms are rigorously removed through a transformation of the basis set (W. J. Hunt et al. [5]) and not through approximations as in the Nesbet's method of symmetry and equivalence restrictions (Proc. Roy. Soc. A230 (1955) 312).

3. CALCULATIONS

All calculations used Gaussian basis functions †. The primitive functions are based on Huzinaga's atomic calculations [7]; nine s-type and five p-type functions on the oxygen atom and four s-type functions on the hydrogen, scaled to 1.2, are included in the primitive set, which is denoted as (95/4). From this set a smaller set of five s-type and three p-type contracted functions on the oxygen atom and three s-type contracted functions on the hydrogen atom was found; this set is denoted as [53/3]. For the [53/3] set we obtain a Hartree-Fock energy of -76.0127 au for the ground state of water - only 0.0005 au higher than the energy for the uncontracted (95/4) set [8]. In addition, properties calculated using the [53/3] set are in close agreement with those predicted by the [95/4] set. For each excited state orbital symmetry, several uncontracted Gaussian basis functions of s and p type were added ††. The coordinate system was chosen so that the molecule is in the yz plane with the z axis extending between the hydrogen atoms.

4. RESULTS

For a Rydberg-type transition, the core orbitals of the upper state should resemble the orbitals of the ion corresponding to removal of the loosely bound electron. Thus the excitation energy should be incorrect by about the error in the ionization potential predicted by Koopman's theorem [1]. But the stability of the excited state relative to ionization should be predicted accurately by the eigenvalue of the excited orbital. These predictions are borne out by the results shown in table 1, where stability indicates the predicted stability with respect to the ion, i.e., $\epsilon_{ii} - \epsilon_{II}$. For example, the experimental and theoretical stabilities for the 1B_1 ($na_1 - 1b_1$) excited states are typically within 0.3 eV of each other. The results using RVO's are also given in table 1; here we see a quite erratic behavior. Note especially that in no case does the lowest RVO correspond to the excited state with the lowest total energy, i.e., lowest ΔE . From table 1 we also see that the s-like states typically

have quantum defects, δ , of 1.3 to 1.4 while the p-like states have quantum defects of 0.7 to 0.8. Exceptions occur for the ${}^3, {}^1A_2$ states which have $\delta \approx 1.1$.

Properties of some of the improved virtual orbitals are also given in table 2. We see that each state is either mainly s-like or mainly p-like and that these symmetries correspond to characteristically different quantum defects. For example, the s-like states have $\langle x^2 \rangle \approx \langle y^2 \rangle \approx \langle z^2 \rangle$ while the p-like states extend much farther in one direction. It is interesting to note that for a typical s-state the dipole moment indicates that the orbital is shifted *toward* the hydrogens while the typical p-state is shifted *away* from the hydrogens. In order to calculate the total dipole moment and other properties for the various excited states, we also include in table 2 the properties for the ground state of H_2O^+ (and H_2O). The total property is obtained by adding the latter number to the orbital expectation value. For example, the dipole moment of the lowest 1B_1 state is -0.757 (-1.92 D).

The oscillator strength for the first (${}^1B_1 \leftarrow {}^1A_1$) transition is calculated as 2.86×10^{-2} by the IVO method and as 5.06×10^{-2} by the RVO method using the lowest energy RVO. In comparison, an experimental value of 3×10^{-2} has been reported [9].

These results suggests that the IVO approach should be useful for describing Rydberg excited states (all of the excited states of H_2O are Rydberg states), and it should also be an improvement over the RVO method for valence excited states. In particular, if diffuse orbitals are present in an RVO calculation, the low-lying RVO's may all be very diffuse even though the molecule should have low-lying valence states (this difficulty should be removed by the use of IVO). Another advantage of the IVO approach is that it allows a different excited state orbital for different transitions and different spins. This should be important for many valence transitions (such as $\pi^* \leftarrow \pi$ transitions).

Several calculations on excited states of H_2O have been reported previously. Ellison and Shull [10] used the $4a_1$ virtual orbital from a minimum basis set of Slater orbitals calculation to construct a 1B_1 excited state wavefunction. However, no diffuse functions were present in the basis set and some integrals were approximated. The ground state energy was far above the Hartree-Fock limit; the calculated oscillator strength for the (${}^1B_1 \leftarrow {}^1A_1$) transition was 1×10^{-6} , and the excitation energy was 11.93 eV. Horsley and Fink [11] recently examined the potential surfaces

† The "MOSES" molecular SCF program, written by M. Geller and L. Sachs [6] and modified by N. Winter and T. Dunning, was modified for these calculations.

†† Orbital exponents and type: for a_1 , O(S): 0.07, 0.0175, 0.0044, O(p_z): 0.05, 0.0125, 0.003125; for b_2 , O(p_x) - same as O(p_z), H(S) - same as O(p_z); for b_1 , O(p_y): 0.02, 0.002, H(p_y): 0.02.

Table 1
 Excitation energies and stabilities for H₂O (in eV)

Transition	n	EXP ^a		δ	IVO		δ	Type of orbital	RVO ΔE (eV)
		ΔE (eV)	Stab.		ΔE (eV)	Stab.			
$3B_1 \leftarrow 1A_1$ ($na_1 \leftarrow 1b_1$)	4				7.88	5.99	1.49	3s	11.70
	5				11.24	2.63	0.73	3p	12.42
	6				11.81	2.06	1.43	4s	11.27
	7				12.66	1.21	0.65	4p	11.57
	8				12.94	0.93	1.18	c	12.21
$1B_1 \leftarrow 1A_1$ ($na_1 \leftarrow 1b_1$)	4	7.50	5.06		8.53	5.34	1.4	3s	11.71
	5	10.0	2.56	0.7	11.32	2.54	0.69	3p	12.43
	6	11.00	1.56	1.0	11.93	1.93	1.35	4s	11.31
	7	11.37	1.19	0.7	12.68	1.18	0.61	4p	11.62
	8	11.75	0.81	1.0	13.04	0.83	0.95	c	12.36
$3A_1 \leftarrow 1A_1$ ($nb_1 \leftarrow 1b_1$)	2				11.01	2.77	0.79	3p	12.64
	3				12.47	1.31	0.77	4p	11.50
$1A_1 \leftarrow 1A_1$ ($nb_1 \leftarrow 1b_1$)	2	10.16	2.40	0.7	11.42	2.36	0.60	3p	12.65
	3	11.49	1.07	0.7	12.51	1.27	0.73	4p	11.67
$3A_2 \leftarrow 1A_1$ ($nb_2 \leftarrow 1b_1$)	2				9.98	3.79	1.11	3p	12.48
	3				12.09	1.69	1.16	4p	11.85
	4				12.82	0.96	1.23	5p	12.48
$1A_2 \leftarrow 1A_1$ ($nb_2 \leftarrow 1b_1$)	2				10.35	3.42	1.01	3p	12.48
	3				12.22	1.55	1.04	4p	11.85
	4				12.87	0.90	1.11	5p	12.58
$3A_1 \leftarrow 1A_1$ ($na_1 \leftarrow 3a_1$)	4				9.82	5.67	1.45	3s	13.35
	5				12.61	2.88	0.83	3p	14.04
	6				13.50	1.99	1.38	4s	12.92
	7				14.21	1.28	0.74	4p	13.17
	8				14.60	0.89	1.09	5s	13.83
$1A_1 \leftarrow 1A_1$ ($na_1 \leftarrow 3a_1$)	4	9.75 ^b	4.60		10.75	4.74	1.30	3s	13.37
	5				13.18	2.31	0.58	3p	14.04
	6				13.69	1.80	1.25	4s	13.06
	7				14.39	1.10	0.48	4p	13.21
	8				15.01	0.48			14.71

^a) Experimental results from ref. [15] except for the state ($4a_1 \leftarrow 3a_1$). A diagram of ref. [16] was used.

^b) Ref. [17].

^c) Mixture of s and p symmetry.

for the first two excited states of H₂O using a Gaussian lobe basis set and Nesbet's method of symmetry and equivalence restrictions. However, the contraction scheme applied to the basis set had insufficient variational freedom to de-

scribe the system properly. La Paglia [12] carried out a perturbation treatment starting from Hartree-Fock Rydberg orbitals for the oxygen. Harada and Murrell [13] started from neon Hartree-Fock orbitals in a similar perturbation

Table 2
Properties of the 1B_1 excited states of H_2O . Atomic units are used and the origin as at the oxygen.

State IVO	$\delta(r)$	z	Property			Type of orbital
			y^2	x^2	z^2	
$4a_1 \leftarrow 1b_1$	0.6895	-1.813	+ 7.011	+ 5.819	+ 7.935	3s
$5a_1 \leftarrow 1b_1$	0.0271	3.373	+13.33	+13.34	+ 30.96	3p
$6a_1 \leftarrow 1b_1$	0.1637	-5.282	+47.92	+47.80	+ 60.30	4s
$7a_1 \leftarrow 1b_1$	0.0037	7.172	+75.94	+75.95	+190.56	4p
$8a_1 \leftarrow 1b_1$	0.1024	-5.755	+73.11	+73.05	+155.65	-
RVO						
$4a_1 \leftarrow 1b_1$	0.0069	-7.509	+67.25	+67.23	+155.60	
$5a_1 \leftarrow 1b_1$	-0.0045	6.845	+85.94	+85.93	+216.64	
$6a_1 \leftarrow 1b_1$	0.0319	-2.895	+43.70	+43.46	+ 75.49	
$7a_1 \leftarrow 1b_1$	0.0526	3.195	+32.97	+32.84	+ 66.65	
$8a_1 \leftarrow 1b_1$	0.0591	-0.902	+12.99	+13.53	+ 30.21	
H_2O^{+a}	294.6	+1.056	+ 6.776	+ 4.186	+ 6.309	
H_2O^b	294.6	+1.056	+ 3.128	5.536	+ 4.297	

a) Properties of H_2O^+ using orbitals from ground state H_2O calculation, with one $1b_1$ removed. Here the nuclear contributions to the dipole moments are included with a minus sign.

b) The ground state of H_2O with the same basis.

treatment. In both cases agreement was fair but the usefulness of the method is limited. Lin and Duncan [14] used a one-center model system in a calculation involving numerous approximations.

Besides being useful for excited state calculations there are many cases where the set of improved virtual orbitals would be useful in ground state calculations. Examples include configuration interaction, perturbation, and Brueckner-Goldstone calculations.

In conclusion, the use of the modified Hartree-Fock Hamiltonian, with the self Coulomb and exchange terms removed, leads to virtual orbitals which are variationally correct approximations to the excited state orbitals of the molecule (for an unrelaxed core). This approach has been tested here on H_2O and found to lead to good excited state wavefunctions. This method may be used on any system for which the Hartree-Fock ground state calculations can be carried out, and thus should be useful in considering the excited states of a wide range of molecules.

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