OPTIMIZED VALENCE CONFIGURATIONS AND THE F_2 MOLECULE*

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The method of optimized valence configurations has been extended to include split-shell correlation and applied to the molecule F_2. It is found (i) that consideration of the correlation of only the so-called valence electrons is sufficient to yield an accurate description of the chemical bond; (ii) that in accordance with the basic assumption of the method there exists a distinct separation in behavior between optimal configurations that represent the extra correlation resulting from molecular bonding and those that will ordinarily be associated with the correlation in separated atoms; and (iii) that the number of significant configurations of the first kind is small and readily obtainable by a sequence of limited multiconfiguration self-consistent field computations, followed by a single configuration interaction involving all new orbitals thus obtained, while those of the latter kind are indeed numerous but are easily accounted for by a suitable perturbation technique.

The method of optimized-valence configurations (OVC)[1-7] has by now been applied to several molecules. The method, which consists in optimizing through the multiconfigurational self-consistent field technique (MCSCF) the configurations that go to improve the description of the interaction of the valence shells with each other, has been found successful as a scheme for achieving a quantitative description of the chemical bond in diatomic molecules. The success can be attributed mostly to the fact that, unlike the usual configuration-interaction (CI) process, the number of meaningful configurations herein is small and provides one with a smooth transition from the Hartree-Fock method.

The reason why the number of significant configurations is small is twofold. The first relates to the natural-spin-orbital nature of the orbitals resulting from the OVC process. The second and more vital reason is that the correlation in atoms, although large compared with the bond energy, changes little during the molecular formation. In general the correlation between the "core" electrons changes so little as the molecule "forms" that it can be completely neglected, while the intershell correlation between the valence and core electrons can at least be neglected to the first approximation. Thus while it is true that a large, almost unmanageable number of configurations is required for a proper representation of the atomic correlation, the correlation that is truly molecular (namely strongly dependent upon the internuclear separation) is adequately represented by only a few. This observation, although not contradicting the recent work of Davidson and Bender[8] on the first-row hydrides, must be weighed against their pessimistic conclusions regarding the many-configuration approach to molecular systems.

In what follows, we briefly outline the new and simplified computational scheme by which we take into account the contribution of the different excitations to the total wave function. Our procedure involves the following steps:

(1) A basis set of functions is chosen by adequately augmenting the one used for the Roothaan-Hartree-Fock (RHF) wave function. The number of additional functions required is usually small.[2]

(2) The RHF orbitals are obtained by solving the usual self-consistant field equations.

(3) The configurations that are necessary to insure that the molecule dissociates formally into Hartree-Fock atoms in their appropriate states are optimally mixed and all orbitals optimized for various internuclear distances using MCSCF techniques.

(4) In addition to the obvious configurations of step (3) there are configurations whose contributions are small at large internuclear separation but increase sharply as the separation decreases. These are constructed and optimized along with the configurations of step (3). Owing to the terms representing their coupling with each other being small compared with those representing their coupling with the configurations from step (3), we have found it a sufficiently accurate procedure to optimize them one by one in the presence of the latter configurations, instead of doing a full-blown MCSCF with all the configurations simultaneously present, which is an expensive and pathologically convergent process when the total number of necessary configurations is large.

(5) The remaining configurations, whose contributions are mainly atomic and vary slowly

with internuclear distance or are too small for inclusion in step (4), are then obtained using a perturbation treatment.

We report below the application of the above method to the molecule F_2. In doing so we present further clarifications and details of the different steps of the method outlined above. We must emphasize, however, that the theory is applicable to any general diatomic molecule, F_2 serving as a good illustration of the different aspects of the method.

We omit details for steps (1) through (3) which have been discussed elsewhere.[1,5,9] These lead to the optimized-double-configuration (ODC) function

$$(\text{core})1\pi_u{}^4 1\pi_g{}^4[a(3\sigma_g{}^2)+b(3\sigma_u{}^2)], \tag{1}$$

where a, b are mixing coefficients and

$$(\text{core}) \equiv 1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2. \tag{2}$$

In step (4) we add the following configurations which represent "split-shell" correlation between the σ and π shells as well as intrashell correlation in the π shell:

$$\begin{aligned}
&(\text{core})1\pi_u{}^3 1\pi_g{}^4 3\sigma_g 3\sigma_u 2\pi_g({}^1\Sigma_u{}^+ \times {}^1\Sigma_u{}^+),\\
&(\text{core})1\pi_u{}^4 1\pi_g{}^3 3\sigma_g 3\sigma_u 2\pi_u({}^1\Sigma_u{}^+ \times {}^1\Sigma_u{}^+),\\
&(\text{core})1\pi_u{}^2 1\pi_g{}^4 3\sigma_g{}^2 3\sigma_u{}^2({}^1\Sigma_g{}^+),\\
&(\text{core})1\pi_u{}^4 1\pi_g{}^2 3\sigma_g{}^2 3\sigma_u{}^2({}^1\Sigma_g{}^+).
\end{aligned} \tag{3}$$

The symbols within brackets refer to the coupling scheme of the open shells. The other coupling scheme ${}^3\Sigma^+ \times {}^3\Sigma^+$ for the first two configurations in (3) contributes very little. Instead of doing a complete MCSCF with the six configurations —two in (1) and four represented by (3)—we froze $3\sigma_g$, $3\sigma_u$ as obtained in step (3) and optimized only $2\pi_u$, $2\pi_g$ as indicated in step (4). This was found to lead to an optimization "error" $<\sim 0.0010$ a.u. at all separations.

In step (5) we obtain the remainder of the correlation pertinent to the bonding. This consists of two kinds of excitations—one representing the remaining part of the correlation that is essentially molecular, the other that represents the correlations among the valence electrons on each center modified by the bonding. This latter needs a different treatment owing to the fact that these excitations are quite numerous even when optimized. Although their individual contributions are small, they add up to a significant effect. Before we describe our techniques to handle these terms, we consider the sort of excitations that we finally selected. The criterion for this selection, of course, depends on the accuracy we are aiming at. In the present calculations we set our limit of accuracy as 0.1 eV in the bonding. We verified that the correlation in the inner shell $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, $2\sigma_u$ (1*s* and 2*s* atomic shells) as well as their cross-shell correlation with valence shells (2*p* atomic shells) does not take any significant part in the bonding to this accuracy. Certainly at internuclear distances smaller than the equilibrium value these correlations show some appreciable changes; however, at such distances the nuclear repulsion overshadows such small changes. Thus we confine ourselves only to the correlation in and between the shells $3\sigma_g$, $3\sigma_u$, $1\pi_u$, $1\pi_g$. The configurations we selected in step (5) are of two types:

Type I(a), $(\text{core})1\pi_{u,g}{}^3 1\pi_{g,u}{}^4 3\sigma_{g,u} m\sigma_{g,u} n\pi_{g,u}({}^1\Sigma^+ \times {}^1\Sigma^+)$, $m>4$, $n>2$;

Type I(b), $(\text{core})1\pi_{u,g}{}^3 1\pi_{g,u}{}^4 3\sigma_{g,u} m\lambda_{g,u} n\pi_{g,u}({}^1\Delta \times {}^1\Delta$, or ${}^3\Delta \times {}^3\Delta$ or, ${}^1\Phi \times {}^1\Phi$, or ${}^3\Phi \times {}^3\Phi$, etc.),
$\lambda \equiv \delta$, φ, $\cdots$, etc. $m>1$, $n>2$;

Type II(a), $(\text{core})1\pi_u{}^4 1\pi_g{}^4 n\sigma_{g,u}{}^2$, $n>4$;

Type II(b), $(\text{core})1\pi_u{}^4 1\pi_g{}^4 (n\pi_{u,g})^2({}^1\Sigma_g{}^+)$, $n>2$.

The symmetry indices g, u are permuted in all different ways subject to the symmetry requirements of the state ${}^1\Sigma_g{}^+$. We now describe the method we have followed to obtain these terms: A second-order perturbation series for the energy

$$\Delta E^{(2)} = -\sum_i \frac{\langle 0|H|i\rangle^2}{E_i - E_0} \tag{4}$$

will involve two types of integrals $\langle 0|H|i\rangle$ corresponding to the two types of configurations shown above. For the Type II functions we have, using Roothaan's[1] expansion formalism and suppressing any constant factor,

$$\langle 0|H|i\rangle = D_{\text{ex}}{}^{\dagger}\mathcal{K} D_{\text{val}}, \tag{5}$$

where $\mathcal{K} \equiv \{K_{pq,rs}\}$ is the exchange supermatrix and $D_{\text{val}}, D_{\text{ex}}$ represent the "density matrices" for the valence and excited shells. For the Type I, let 1, 2 represent valence shells and 3, 4 the excited shells. Then, again in expansion formalism and suppressing constant factors,

$$\langle 0|H|i\rangle = D_{12}{}^{\dagger}\mathcal{J}D_{34}, \qquad (6)$$

where D_{ij} is a cross-shell density matrix given by

$$D_{ij,pq} = C_{ip}C_{jq}, \qquad (7)$$

and $\mathcal{J}$ is some linear combination of the Coulomb and exchange supermatrices.[10] A fast convergence of the series (4) can be secured if $|i\rangle$'s are obtained such that the corresponding term in the series is a maximum under the constraints of orthogonality to all the orbitals obtained already. We prefer, however, to extremize just $\langle 0|H|i\rangle$ for getting these orbitals. We thereby avoid the lengthy iterative processes; further it is not necessary to obtain $|i\rangle$ for each term of the series. Only one extremization for each type will yield all the excited orbitals as eigenfunctions belonging to the respective type. Let us consider the equation to extremize the coupling represented by Eq. (5):

$$\mathcal{K}D_{\text{val}}C_{\text{ex}} = \epsilon S C_{\text{ex}} + \sum \epsilon_j S C_j, \qquad (8)$$

where S is the overlap matrix and the ϵ's are the usual Lagrangian multipliers arising from the constraints of orthonormality. It is clear that since we do not propose to alter D_{val}, the solution of Eq. (8) is noniterative and can be performed immediately. A similar situation holds in the Type-II case. Let us first assume that C_3, C_4 belong to different symmetry species λ and λ'. Then the equations to maximize coupling (6) are given by

$$M_{\lambda\lambda'}C_4 = S_\lambda C_3 + \sum_j{}^{(\lambda)}\epsilon_{3j}S_\lambda C_j,$$
$$M_{\lambda\lambda'}{}^{\dagger}C_3 = S_{\lambda'}C_4 + \sum_j{}^{(\lambda')}{}_{4j}S_{\lambda'}C_j, \qquad (9)$$

where the summations are over all orbitals belonging respectively to λ and λ' excluding C_3 and C_4. $M_{\lambda\lambda'}$ is given by

$$M_{\lambda p,\lambda' q} = \sum_{rs}\mathcal{J}_{\lambda p\lambda' q,\mu r\mu' s}D_{12rs},$$

with μ, μ' being the symmetry species of 1 and 2, respectively. After an easy manipulation Eqs. (5) are uncoupled to yield

$$M_{\lambda\lambda'}{}^{\dagger}(S_\lambda{}^{-1} - \sum_j{}^{(\lambda)}C_jC_j{}^{\dagger})M_{\lambda\lambda'}C_4 = \epsilon^2 S_{\lambda'}C_4,$$
$$M_{\lambda\lambda'}(S_{\lambda'}{}^{-1} - \sum_j{}^{(\lambda')}C_jC_j{}^{\dagger})M_{\lambda\lambda'}{}^{\dagger}C_3 = \epsilon^2 S_\lambda C_3, \qquad (10)$$

which can be immediately solved. When C_3, C_4 are of the same symmetry species it can be shown that their linear combinations

$$u = C_3 + C_4, \quad v = C_3 - C_4,$$

satisfy

$$Mu = \epsilon S u, \quad Mv = \epsilon' S v,$$

provided the supermatrix in Eq. (6) is symmetric.

We report below the results of calculations on F_2, carried out along the above lines. The basis set used in these calculations is slightly inferior (0.001 a.u. in the hf energy) to the one used in earlier reports. This choice of the basis set (namely a common basis set for g and u symmetries) was motivated primarily by economic considerations. The basis set, which consists of 18 σ functions and 10 π functions, rules out the Type I(b) excitations automatically, although on the

Table I. Energy analysis.

Contributing terms \ Internuclear separation (a.u.)	1.8	2.2	2.68	3.0	3.5	6.0
Two Main Configs. (i.e. $3\sigma_g{}^2$ & $3\sigma_u{}^2$)	-198.4324	-198.7679	-198.84287	-198.84193	-198.8296	-198.8178
Col. 4 of Table IX, Ref. 5	-198.4454	-198.7772	-198.84853	-198.84551	-198.83094	-198.8180
Basis function & extra molecular correlation correction	-.0130	-.0093	-.0056	-.0036	-.0013	-.0002
/6-Conf. function	-198.4760	-198.8171	-198.8834	-198.8716	-198.8437	-198.8178
The atomic correlation terms	-.0394	-.0325	-.0253	-.0250	-.0286	-.0384
Total energy	-198.5284	-198.8589	-198.9143	-198.9002	-198.8736	-198.8564

basis of atomic correlation energies and other numerical checks we believe that individual contributions from the excitations considered cannot be off by more than 10% of their calculated values.

Table I gives the energy versus internuclear distance for the various sets of configurations. The first row gives the double-configuration [Eq. (2)] values with the present basis set. They differ slightly from the values of Ref. 5 owing to the difference in the basis sets. The second row gives 8-configuration values of the same reference and the difference between the first and second rows given in the third row will be used to correct for the basis set as well as for the fact that we have not included any Type-II excitations in the present calculations. The fourth row gives the values for the 6-configuration function discussed above. The fifth row gives the contributions from the "atomic" excitations. The sixth row gives the energy values for our final potential curve. The Dunham's analysis of this curve yields the spectroscopic values given in Table II. As to comparison with experiment, we make the following remarks: First, our wave function lacks completely in Type I(b) configurations which from independent evidence should contribute of the order of 0.01 a.u. at the separated-atom limit. We can make some rough estimate of how much of this goes into the binding energy. We observe that at large internuclear distances $4\sigma_g$, $4\sigma_u$, $3\pi_u$, $3\pi_g$ are atomic $3p$ functions while $5\sigma_g$, $5\sigma_u$, $4\pi_u$, $4\pi_g$ are $3d$ functions. We can expect that it is the same $3d$ functions which will be involved in the Type I(b) excitation involving a δ-species excited orbital. Thus we argue that the R dependence of these excitations will be as strong as that of any of the excitations $3\sigma_g 1\pi_{g,u} 4\pi_{g,u}$. From atomic results the $2p\sigma$-$2p\pi$ correlation in two F atoms is ~0.05 a.u. Thus the Type I(b) excitations could contribute ~0.01 a.u. at large R and, using Table II for the $3\sigma_g 1\pi_{g,u} 5\sigma_{g,u} 4\pi_{g,u}$ excitations, ~0.003 a.u. at $R = 2.68$. This indicates that the inclusion of such excitations would lower our binding energy; however, improvements in the basis set and orbital optimization will certainly raise the value of 1.57 eV. In considering the counterbalance effects we feel that the results support a binding energy for F_2 of 1.6 eV and do not support the recent value of 1.39 eV (see Table II).

We have thus shown above how to quantitatively separate out and evaluate the "molecular" aspects of the system of two approaching atoms (by means of a series of limited MCSCF computations yielding a set of optimal orbitals which are then employed in a larger CI calculation) and how to take account of remaining correlation which can be labeled as "atomic" (by a modified perturbation approach). We feel that such a separation is of paramount importance in making quantitative predictions about the chemical bond and energy surfaces particularly as the arduous search for tractable methods of attacking the correlation problem is extended to larger molecules.

Table II. Spectroscopic constants.

Source	r_e (a.u.)	D_e (eV)	ω_e (cm^{-1})
This calculation	2.59	1.57	1021
Experimental	2.68[a]	1.39 ±0.03[b]	892[g]
		1.49 ±0.07[c]	
		1.68 ±0.09[d]	
		1.65 ±0.05[e]	
		1.65[f]	

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[10] In dealing with cross-shell excitations, one has to consider types of integrals which are antisymmetric in the interchange of orbital indices belonging to the same symmetry in addition to the ones usually occurring in expansion formalism that are symmetric in such indices. However, these antisymmetric integrals are generally small compared with the corresponding symmetric ones.