

Table 1.2 Formal scaling of computational cost with the size of the orbital space, m . $iter-m^x$ indicates there are many iterative steps, each of computational cost m^x .

<i>Method:</i>	<i>HF</i>	<i>MP2</i>	<i>CISD</i>	<i>CCSD</i>	<i>CCSD(T)</i>	<i>FCI</i>
Formal Scaling	$iter-m^4$	m^5	$iter-m^6$	$iter-m^6$	$iter-m^6+m^7$	$m!$
Variational?	Yes	No	Yes	No	No	Yes
Size-consistent?	Yes	Yes	No	Yes	Yes	Yes

formal cost of the methods we have discussed, assuming no approximations, and this does provide a useful comparison, see Table 1.2.

1.4.5 Multiconfigurational and Multireference Methods

The families of correlated methods we have described so far all depend on the Hartree-Fock determinant dominating the final wavefunction, that is $C_0 \approx 1$ in eqn (1.67), and all the many other determinants providing a relatively small, but essential, component of the total wavefunction. In certain systems the reference wavefunction cannot be represented adequately by a single Slater determinant. Such situations arise, for example, when chemical bonds are stretched or when spin-paired electrons occupy energetically degenerate but spatially distinct orbitals. Consider the familiar molecular orbital picture of an electron pair bond between two identical atoms, in which atomic orbitals on the two atoms mix to form bonding and antibonding molecular orbitals, as shown in Figure 1.18a. If the bond between atom *A* and atom *B* is stretched, the energy separation between the bonding and antibonding molecular orbitals is reduced, as in Figure 1.18b. If the atoms are moved to very large separation, as might be required when calculating a diatomic potential energy curve, the bonding and antibonding combinations will become degenerate. In the first case, Figure 1.18a, it is obvious that the two electrons should be placed in the lower lying bonding orbital. In the final case, Figure 1.18c, there is no reason to place the electrons in the bonding orbital, since now it is degenerate with the antibonding orbital. In such situations we must include two determinants: one with the bonding orbital doubly occupied and the other with the antibonding orbital doubly occupied. This is the extreme case of exact degeneracy and we would expect each Slater determinant to contribute equally to the wavefunction. This is easily illustrated with the simple case of the hydrogen molecule described with a minimal basis set consisting of a single *1s* type function on each atom. The problem arises in the Hartree-Fock method because, even at dissociation, both electrons are assigned to a single symmetric doubly occupied molecular orbital of the form

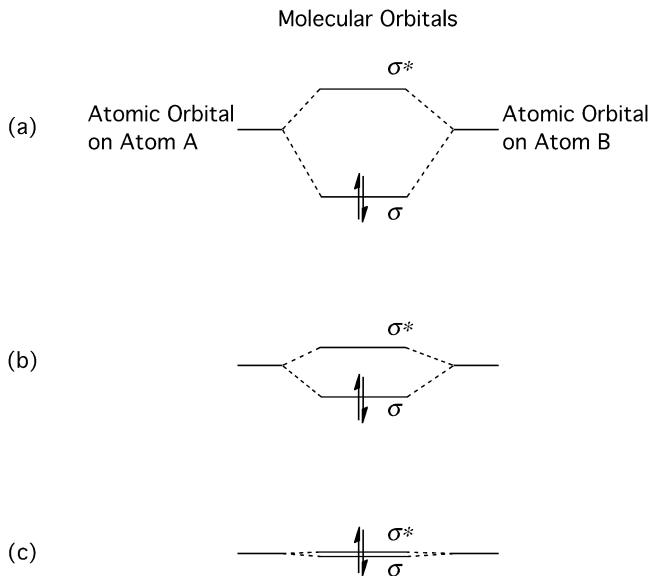


Figure 1.18 (a) Homonuclear diatomic bonding and antibonding orbital energy levels at equilibrium bond distance. (b) Bonding and antibonding energy levels at stretched bond distance. (c) Bonding and antibonding energy levels for completely separated atoms.

$$\sigma = \frac{1}{\sqrt{2}} [\chi_A + \chi_B] \quad \text{H}_A \cdots \cdots \text{H}_B \quad (1.83)$$

where χ_A is the $1s$ type function on atom A , and χ_B that on atom B . The corresponding Slater determinant is

$$|\Psi_0\rangle = |\sigma\bar{\sigma}\rangle = \frac{1}{\sqrt{2}} \sigma(\mathbf{r}_1)\sigma(\mathbf{r}_2)[\alpha(\mathbf{s}_1)\beta(\mathbf{s}_2) - \beta(\mathbf{s}_1)\alpha(\mathbf{s}_2)] \quad (1.84)$$

Regardless of the internuclear distance, the form of the bonding orbital remains that given in eqn (1.83). The spatial part of the wavefunction can be expanded to give

$$\sigma(\mathbf{r}_1)\sigma(\mathbf{r}_2) = \frac{1}{2} [\chi_A(\mathbf{r}_1)\chi_A(\mathbf{r}_2) + \chi_A(\mathbf{r}_1)\chi_B(\mathbf{r}_2) + \chi_B(\mathbf{r}_1)\chi_A(\mathbf{r}_2) + \chi_B(\mathbf{r}_1)\chi_B(\mathbf{r}_2)] \quad (1.85)$$

According to this the two electrons spend half of their time on different atoms, one on atom A and one on atom B , and the other half of their time on one atom, either atom A or atom B . In terms of structures, even at dissociation, the wavefunction contains 50% $\text{H}_A \bullet \bullet \text{H}_B$, 25% $\text{H}_A^- + \text{H}_B$ and 25% $\text{H}_A^+ - \text{H}_B$. This is

clearly incorrect, since the molecule should dissociate into $2\text{H}\cdot$. The correct form required for the wavefunction at dissociation is

$$\frac{1}{2}[\chi_A(\mathbf{r}_1)\chi_B(\mathbf{r}_2) + \chi_B(\mathbf{r}_1)\chi_A(\mathbf{r}_2)][\alpha(\mathbf{s}_1)\beta(\mathbf{s}_2) - \beta(\mathbf{s}_1)\alpha(\mathbf{s}_2)] \quad (1.86)$$

This form of the wavefunction cannot be expressed as a single determinant. However if we use the antibonding orbital

$$\sigma^* = \frac{1}{\sqrt{2}}[\chi_A - \chi_B] \quad (1.87)$$

and expand the spatial component of the corresponding determinant

$$\sigma^*(\mathbf{r}_1)\sigma^*(\mathbf{r}_2) = \frac{1}{2}[\chi_A(\mathbf{r}_1)\chi_A(\mathbf{r}_2) - \chi_A(\mathbf{r}_1)\chi_B(\mathbf{r}_2) - \chi_B(\mathbf{r}_1)\chi_A(\mathbf{r}_2) + \chi_B(\mathbf{r}_1)\chi_B(\mathbf{r}_2)] \quad (1.88)$$

We can see that the $\text{H}_A\cdot\cdot\text{H}_B$ type terms occur with the opposite sign to that in eqn (1.85). If we subtract the determinants we obtain the required form for dissociated hydrogen

$$|\sigma\bar{\sigma}\rangle - |\sigma^*\bar{\sigma}^*\rangle = \frac{1}{2}[\chi_A(\mathbf{r}_1)\chi_B(\mathbf{r}_2) + \chi_B(\mathbf{r}_1)\chi_A(\mathbf{r}_2)][\alpha(\mathbf{s}_1)\beta(\mathbf{s}_2) - \beta(\mathbf{s}_1)\alpha(\mathbf{s}_2)] \quad (1.89)$$

In the intermediate situation of stretched bond lengths, we will not have exact degeneracy, but can speak of near-degeneracy of the bonding and antibonding orbitals. The contribution of the doubly substituted determinant, eqn (1.88), will not be 50% of the wavefunction but it will be significant. We can summarise the three situations depicted in Figure 1.18 for the case of the hydrogen molecule by writing a CI type wavefunction

$$|\Psi_{\text{CI}}\rangle = C_1|\sigma\bar{\sigma}\rangle + C_2|\sigma^*\bar{\sigma}^*\rangle \quad (1.90)$$

At equilibrium, Figure 1.18a, $C_1 \gg C_2$ ($C_1 \approx 1, C_2 \approx 0$). At stretched bond distances, Figure 1.18b, $C_1 > C_2$ and at dissociation, Figure 1.18c, $C_1 = C_2$. In the latter two circumstances the qualitatively correct wavefunction is not given by eqn (1.84), but rather by eqn (1.90). It consists of more than one Slater determinant and is said to be multiconfigurational in character. Figure 1.19 shows the potential energy curve for molecular hydrogen calculated using eqns (1.84) and (1.90). The difference between the two curves in Figure 1.19 is a type of electron correlation energy, it is highly structure dependent and is termed non-dynamic electron correlation. The non-dynamic electron correlation comes from the inability of a single determinant to provide a qualitatively correct reference wavefunction. In Figure 1.19, if we were to adopt the definition of eqn (1.64) for the correlation energy, we can see that as the bond distance increases the correlation energy also increases, reaching a maximum

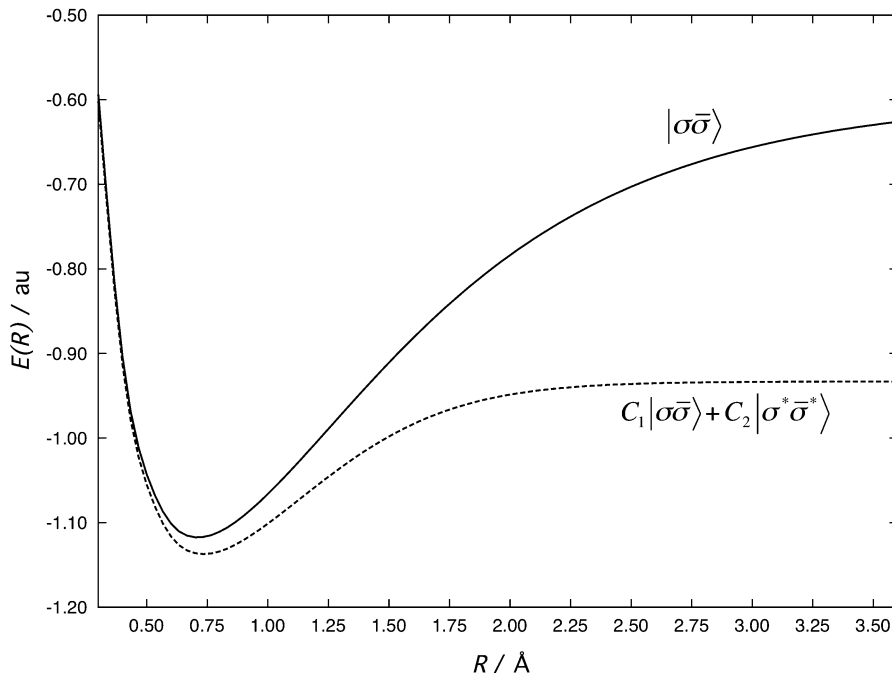


Figure 1.19 Potential energy curve for H_2 using the wavefunction forms given in eqns (1.84) (solid line) and (1.90) (dashed line).

value at dissociation! This is clearly nonsensical, since at dissociation we have two separated hydrogen atoms and there must be no electron correlation. In this case the correct reference wavefunction is given by eqn (1.90), since at dissociation eqn (1.84) describes a physically incorrect wavefunction.

The orbitals where near-degeneracy effects operate may be a very small subset of the full orbital space. The majority of the orbitals will be adequately described as doubly occupied or empty. To define an appropriate reference wavefunction we must optimise the orbitals, as in the Hartree-Fock method, but also allow a mixing of determinants, as in eqn (1.90), so that optimal mixing coefficients may be determined through minimisation of the energy. This is the realm of the multiconfigurational SCF (MCSCF) method. To proceed we partition the orbital space into three subspaces. The first subspace, termed “inactive”, consists of orbitals that remain doubly occupied in all determinants. The second subspace, termed “active”, consists of orbitals that are allowed to have variable occupancy through the mixing of determinants. The third subspace is the “virtual” space and contains orbitals that are unoccupied in all determinants. Returning to the lithium hydride example, with its four electrons in three molecular orbitals (ϕ_1, ϕ_2, ϕ_3) built from a basis set consisting of a $1s$ function on hydrogen and a $1s$ and $2s$ function on lithium, we could choose the inactive subspace to consist of the ϕ_1 orbital (essentially the $1s$ orbital on lithium) and the active subspace to be the ϕ_2 and ϕ_3 bonding

and antibonding orbitals. In this limited basis there will be no virtual orbital subspace. The active space consists of two electrons and two orbitals, if we allow all possible distributions of the active electrons in the active orbitals for an overall $S = 0$ then we shall have a complete active space (CAS). The CAS will comprise the four determinants shown in Figure 1.20.

Keeping ϕ_1 as doubly occupied in all configurations has reduced the number of determinants from nine (Figure 1.16) to four (Figure 1.20). However if we were to consider the same approach for, say the nitrogen molecule, the number of active orbitals would have to include, at least, each bonding and antibonding orbital of the triple bond. The active space would now include six electrons and six orbitals and the CAS would involve 400 determinants. This small extension of the active space results in a dramatic increase in the number of determinants involved.

Multi-configurational methods are conceptually and computationally much more difficult than the single determinant Hartree-Fock method. For diatomic molecules the choice of active space is simple. However for general molecular systems, especially in chemical reactions, great care must be exercised in the choice of active space to keep it small enough to ensure that the calculation remains computationally tractable but flexible enough to adequately describe the chemical situation being explored. Provided that a suitable active space can be chosen, the orbitals are optimised in a similar fashion to the Hartree-Fock method. This defines a suitable reference wavefunction that can then be subjected to further elaboration using CI, Møller-Plesset or CC methods to account for the dynamic correlation energy. The techniques we have discussed for correlated calculations can all be extended to the case of multiconfigurational reference wavefunctions. Such multireference techniques (MR-CI, MR-MP2, MR-CC) are very much more computationally demanding but their use is sometimes essential in order to arrive at meaningful results.

Multi-configurational and multi-reference methods are not as widely used as their single-determinant-based counterparts. The calculations do require greater computational resources but perhaps more importantly they require a high degree of chemical understanding on the part of the user if they are to produce useful studies. The choice of active space provides a great degree of flexibility in the application of multi-reference techniques. This means that they are, in principle,

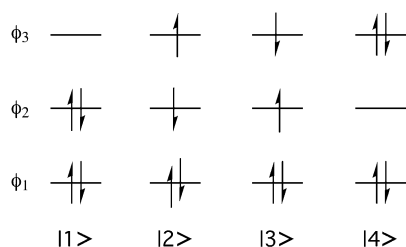


Figure 1.20 Complete active space (CAS) determinants for two electrons in two orbitals and $S = 0$.

applicable to any type of chemical structure but in practice the pragmatic choice of active space provides the opportunity for erroneous modeling. These are not automatic ‘black-box’ techniques and should be used with due care and caution.

1.4.6 Density Functional Methods

The final type of standard model we shall discuss is that based on density functional theory (DFT). These are currently the most widely used techniques for the study of general chemical problems. The ultimate aim is to deal directly with the one-electron density and circumvent consideration of the many-electron wavefunction. An N -electron wavefunction, $|\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\rangle$, contains all information on the system and depends on $4N$ coordinates, that is three spatial and one spin coordinate per electron. A remarkable theorem due to Hohenberg and Kohn establishes that the ground state energy and all ground state properties can be obtained from functionals of the one-electron density alone. Formally, the one-electron density, $\rho(\mathbf{r})$, can be obtained from the N -electron wavefunction, $|\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\rangle$, by integrating over all electronic spin coordinates and over all spatial coordinates, except those of electron 1.

$$\rho(\mathbf{r}_1) = N \int |\psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\mathbf{s}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \quad (1.91)$$

Consequently $\rho(\mathbf{r}_1)$ depends only on the three spatial coordinates of electron 1, regardless of the number of electrons in the system. If we can work with $\rho(\mathbf{r}_1)$ as a fundamental quantity, instead of $|\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)\rangle$, it should lead to less demanding computations. Additionally it provides us with a simple quantity defined in three-dimensional physical space to deal with, rather than the many-dimensional space of the N -electron wavefunction.

Unfortunately the Hohenberg-Kohn theorem does not tell us how we might find suitable functionals of $\rho(\mathbf{r}_1)$. To proceed we can make use of the known exact solution to an idealised electronic problem, that of the uniform electron gas. The ‘‘uniform’’ refers to the distribution of the electron density throughout the gas. The Coulomb and Fermi correlation properties of the uniform electron gas can be extracted in the form of exchange (Fermi) – correlation (Coulomb) functionals of the one-electron density. These exchange-correlation functionals can be added to a self-consistent field type formalism providing a computationally efficient technique. This approach, with suitable modifications, is capable of wide application and good accuracy for chemical problems. Modifications and refinements are necessary since the uniform electron gas is generally not a good approximation to the electron distribution in chemical systems. For example, the electron distribution around two bonded atoms of very different electronegativity will produce a very non-uniform distribution of the electron density. Many formal results in DFT are known and formal developments in the theory continue. If the exact form of the exchange and correlation terms was known for

number of electrons, does not have all its electrons paired. The molecular orbitals of homonuclear diatomics are ordered $1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u, (3\sigma_g, 1\pi_u), 1\pi_g, 3\sigma_u$. The last two electrons of O_2 go into the doubly degenerate anti-bonding $1\pi_g$ orbital. By Hund's rule, these two electrons go into separate $1\pi_g$ orbitals with their spins parallel so as to enjoy the negative exchange interaction. This, therefore, leads to a final ${}^3\Sigma_g^-$ state. The occupied orbitals of an unrestricted 6-31G* calculation on O_2 , for a bond length of 2.281 a.u., are shown in Fig. 3.15. The "open-shell" alpha electrons in the $1\pi_g$ orbital "push" down (stabilize) the α orbitals relative to the β orbitals because of exchange interactions that are present only between electrons of the same spin. In a restricted description, all but the $1\pi_g$ orbitals would be constrained to be paired. Note how the order of the $1\pi_u$ and $3\sigma_g$ orbitals are reversed for electrons of α and β spin.

To complete our discussion of unrestricted Hartree-Fock theory, we will use our minimal basis H_2 model to investigate the description of bond dissociation by unrestricted wave functions.

3.8.7 The Dissociation Problem and Its Unrestricted Solution

The unrestricted wave function is normally used to describe open-shell states—doublets, triplets, etc., as in the examples of the last subsection. Under certain circumstances, however, it may be appropriate to use an unrestricted wave function to describe states that are normally thought of as closed-shell singlets. For the ground state of a molecule like H_2 , the restricted formulation, with electrons paired, is the usual description. As we shall shortly see, it is also the only appropriate Hartree-Fock description under certain conditions. At very large bond lengths, however, one is really trying to describe two individual hydrogen atoms. A proper description will have one electron on one H atom and the other electron on the other H atom, i.e., the two electrons will have quite different spatial distributions. They should not have identical spatial distributions as is implied by a restricted wave function, which places both electrons in the same spatial orbital. It would thus appear that at equilibrium distances we want a restricted wave function, but at large bond lengths we want an unrestricted wave function. In a sense, we will be able to have our cake and eat it too. As was discussed in the previous subsection, there may exist two solutions to the unrestricted equations of Pople and Nesbet when $N^\alpha = N^\beta$. The restricted solution of Roothaan's equations is necessarily a solution to the Pople-Nesbet equations. It only remains to discover whether there is a second truly unrestricted solution that is lower in energy than the restricted solution. We shall find that for normal geometries there is not always an unrestricted solution. If, however, we stretch a bond which cleaves homolytically, like the bond in H_2 ($H_2 \rightarrow H + H$) but unlike the bond in HeH^+ ($HeH^+ \rightarrow He + H^+$), then an unrestricted solution will always exist at large bond lengths. The unrestricted solution

accommodates the unpairing of electrons inherent in the breaking of the bond. To see this explicitly, we will investigate wave functions for our minimal basis model of H_2 .

We could numerically solve the Pople-Nesbet equations for minimal basis STO-3G H_2 , just as we have solved them for CH_3 , N_2^+ , and O_2 . An appropriate unrestricted initial guess would be required if the iterations were to lead to an unrestricted solution rather than to the restricted solution. The transition from a restricted to an unrestricted wave function will be more transparent, however, if, rather than obtain a numerical solution to the Pople-Nesbet matrix equations, we formulate the problem in an analytical fashion.

The restricted molecular orbitals of minimal basis H_2 are symmetry determined and given by

$$\psi_1 = [2(1 + S_{12})]^{-1/2}(\phi_1 + \phi_2) \quad (3.356)$$

$$\psi_2 = [2(1 - S_{12})]^{-1/2}(\phi_1 - \phi_2) \quad (3.357)$$

Since the minimal basis model has only two basis functions with coefficients that can be varied and since molecular orbitals are constrained to be normalized, the minimal basis model has, in the general case, only one degree of freedom. An unrestricted solution, unlike the restricted solution, is not symmetry determined and a convenient way of incorporating this one degree of freedom into unrestricted calculations is to write the unrestricted occupied molecular orbitals ψ_1^α and ψ_1^β as linear combinations of the restricted symmetry determined orbitals ψ_1 and ψ_2 , as follows:

$$\psi_1^\alpha = \cos \theta \psi_1 + \sin \theta \psi_2 \quad (3.358)$$

$$\psi_1^\beta = \cos \theta \psi_1 - \sin \theta \psi_2 \quad (3.359)$$

The single degree of freedom here is in the angle θ . It is sufficient to consider values of θ between 0° and 45° . The value $\theta = 0$ corresponds to the restricted solution $\psi_1^\alpha = \psi_1^\beta = \psi_1$ and nonzero values of θ correspond to unrestricted solutions $\psi_1^\alpha \neq \psi_1^\beta$. The unrestricted virtual orbitals are given by

$$\psi_2^\alpha = -\sin \theta \psi_1 + \cos \theta \psi_2 \quad (3.360)$$

$$\psi_2^\beta = \sin \theta \psi_1 + \cos \theta \psi_2 \quad (3.361)$$

Exercise 3.42 Show that the set of α orbitals $\{\psi_1^\alpha, \psi_2^\alpha\}$ and the set of β orbitals $\{\psi_1^\beta, \psi_2^\beta\}$ form separate orthonormal sets.

If we substitute the basis set expansions (3.356) and (3.357) into the previous four equations, we will obtain basis set expansions for the unrestricted molecular orbitals. The occupied molecular orbitals, which are the

only ones we need consider from now on, are given by

$$\psi_1^\alpha = c_1\phi_1 + c_2\phi_2 \quad (3.362)$$

$$\psi_1^\beta = c_2\phi_1 + c_1\phi_2 \quad (3.363)$$

where

$$c_1 = [2(1 + S_{12})]^{-1/2} \cos \theta + [2(1 - S_{12})]^{-1/2} \sin \theta \quad (3.364)$$

$$c_2 = [2(1 + S_{12})]^{-1/2} \cos \theta - [2(1 - S_{12})]^{-1/2} \sin \theta \quad (3.365)$$

By allowing ψ_2 to mix with ψ_1 in the definition of the unrestricted occupied orbitals (Eqs. (3.358) and (3.359)), we allow the weights of ϕ_1 and ϕ_2 in the basis set expansions of ψ_1^α and ψ_1^β to vary as shown by Eqs. (3.362) and (3.363). If $\theta = 0$, the wave function is just the restricted wave function with $c_1 = c_2 = [2(1 + S_{12})]^{-1/2}$. As θ increases from zero, c_1 gets larger and c_2 gets smaller or, equivalently, ψ_1^α acquires a larger admixture of ϕ_1 and ψ_1^β acquires a larger admixture of ϕ_2 . If $S_{12} = 0$ as is appropriate for large internuclear distances, then in the limit of $\theta = 45^\circ$ we have $c_1 = 1$, $c_2 = 0$, and

$$\left. \begin{array}{l} \psi_1^\alpha \equiv \phi_1 \\ \psi_1^\beta \equiv \phi_2 \end{array} \right\} \theta = 45^\circ, \quad S_{12} = 0 \quad (3.366)$$

This is the result we desire for two separate H atoms—an electron with α spin in ϕ_1 and an electron with β spin in ϕ_2 .

We thus characterize molecular orbitals for minimal basis H_2 by the single parameter θ . At one extreme, $\theta = 0$ corresponds to the restricted solution where the occupied molecular orbital is an equal mixture of ϕ_1 and ϕ_2 . At the other extreme, $\theta = 45^\circ$ corresponds to an unrestricted solution for isolated hydrogen atoms. Intermediate value of θ correspond to unrestricted solutions where ψ_1^α is mainly ϕ_1 and ψ_1^β is mainly ϕ_2 . Figure 3.16 gives a qualitative picture of the unrestricted molecular orbitals of H_2 as a function of θ . While we have derived this picture using the minimal basis, the figure is qualitatively correct for H_2 with any basis set.

We have seen that for the ground state of a closed-shell molecule like H_2 it appears possible to define unrestricted wave functions which have the qualitatively correct behavior that we expect for the dissociation process. It remains to relate these unrestricted wave functions to solutions of the Hartree-Fock equations. If we solve the Pople-Nesbet equations, will a non-zero value of θ be obtained? To investigate this question, we need to determine the energy as a function of θ .

The electronic energy of an unrestricted single determinant wave function for H_2 ,

$$|\Psi_0\rangle = |\psi_1^\alpha(1)\bar{\psi}_1^\beta(2)\rangle \quad (3.367)$$

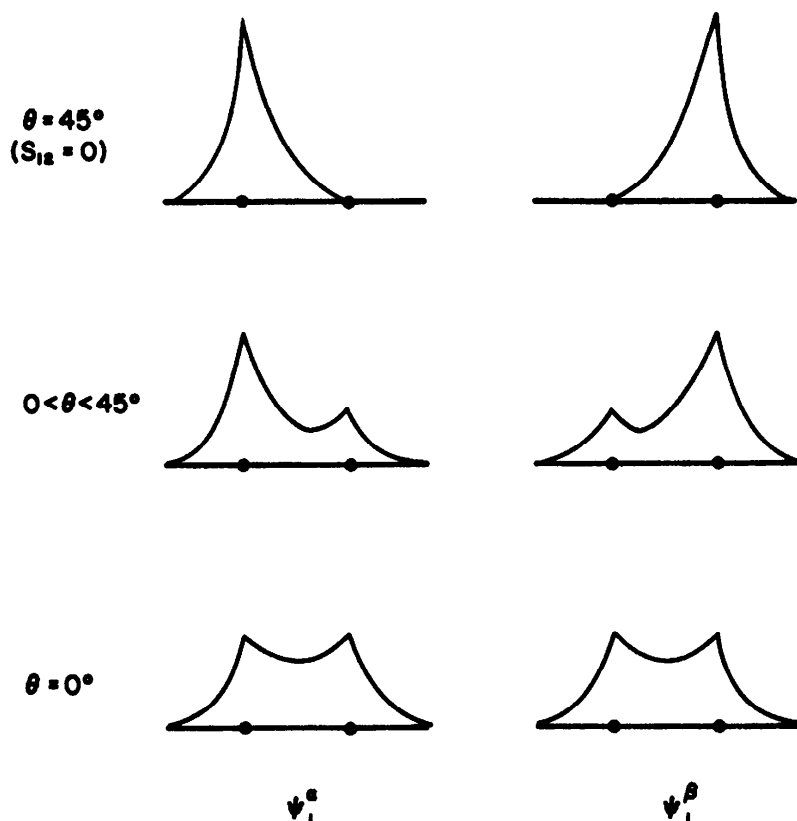


Figure 3.16 Qualitative behavior of unrestricted molecular orbitals ψ_1^α and ψ_1^β for H_2 as a function of θ .

is just the kinetic energy and nuclear attraction of each electron, plus the coulomb repulsion between the two electrons. That is,

$$\begin{aligned} E_0 &= \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = h_{11}^\alpha + h_{11}^\beta + J_{11}^{\alpha\beta} \\ &= (\psi_1^\alpha | h | \psi_1^\alpha) + (\psi_1^\beta | h | \psi_1^\beta) + (\psi_1^\alpha \psi_1^\alpha | \psi_1^\beta \psi_1^\beta) \end{aligned} \quad (3.368)$$

Substituting the expansions (3.358) and (3.359) into this expression, we can write the electronic energy, as a function of θ , in terms of molecular integrals of the restricted problem

$$\begin{aligned} E_0(\theta) &= 2 \cos^2 \theta h_{11} + 2 \sin^2 \theta h_{22} + \cos^4 \theta J_{11} \\ &\quad + \sin^4 \theta J_{22} + 2 \sin^2 \theta \cos^2 \theta (J_{12} - 2K_{12}) \end{aligned} \quad (3.369)$$

If $\theta = 0$, the unrestricted energy just reduces to the restricted energy

$$E_0(0) = 2h_{11} + J_{11} \quad (3.370)$$

The first derivative of the unrestricted energy with respect to θ is

$$\begin{aligned} dE_0(\theta)/d\theta &= 4 \cos \theta \sin \theta [h_{22} - h_{11} + \sin^2 \theta J_{22} - \cos^2 \theta J_{11} \\ &\quad + (\cos^2 \theta - \sin^2 \theta)(J_{12} - 2K_{12})] \end{aligned} \quad (3.371)$$

To find the values of θ which solve the Pople-Nesbet equations, i.e., to find the values of θ which make the unrestricted energy stationary, we set

the first derivative of the unrestricted energy to zero,

$$dE_0(\theta)/d\theta = AB = 0 \quad (3.372)$$

where

$$A = 4 \cos \theta \sin \theta \quad (3.373)$$

and

$$B = h_{22} - h_{11} + \sin^2 \theta J_{22} - \cos^2 \theta J_{11} + (\cos^2 \theta - \sin^2 \theta)(J_{12} - 2K_{12}) \quad (3.374)$$

There are thus two ways the energy could be stationary:

1. $A = 0$. This is the restricted solution. The condition is satisfied if $\theta = 0$.
2. $B = 0$. This is the unrestricted solution. The condition is satisfied and there exists an unrestricted wave function only if there is a solution to:

$$\cos^2 \theta = \eta \quad (3.375)$$

where

$$\eta = (h_{22} - h_{11} + J_{22} - J_{12} + 2K_{12}) / (J_{11} + J_{22} - 2J_{12} + 4K_{12}) \quad (3.376)$$

This last equation is obtained by setting B of Equation (3.374) to zero. This equation has a solution only if the internuclear distance and basis functions, and hence the molecular integrals h_{11} , h_{22} , etc., are such that η lies between zero and one, i.e., $0 \leq \eta \leq 1$.

Exercise 3.43 Use the molecular integrals given in Appendix D to show that no unrestricted solution exists for minimal basis STO-3G H_2 at $R = 1.4$ a.u. Repeat the calculation for $R = 4.0$ a.u. and show that an unrestricted solution exists with $\theta = 39.5^\circ$. Remember that $\varepsilon_1 = h_{11} + J_{11}$ and $\varepsilon_2 = h_{22} + 2J_{12} - K_{12}$.

To proceed with the analysis let us investigate the nature of the restricted solution ($\theta = 0$) by evaluating the second derivative of the energy (at the restricted solution),

$$\begin{aligned} d^2E_0(\theta)/d\theta^2]_{\theta=0} &= E_0''(0) = 4(h_{22} - h_{11} - J_{11} + J_{12} - 2K_{12}) \\ &= 4(\varepsilon_2 - \varepsilon_1 - J_{12} - K_{12}) \end{aligned} \quad (3.377)$$

The nature of the restricted solution is determined by this second derivative. If $E_0''(0) > 0$, it is an energy minimum. If $E_0''(0) < 0$, it is an energy maximum. If $E_0''(0) = 0$, i.e., if

$$h_{22} - h_{11} = J_{11} - J_{12} + 2K_{12} \quad (3.378)$$

then the restricted solution is a saddle point. Substituting this last saddle point condition into Eq. (3.376), we find that $\eta = 1$ at the saddle point. Using the molecular integrals of Appendix D we can investigate the behavior of

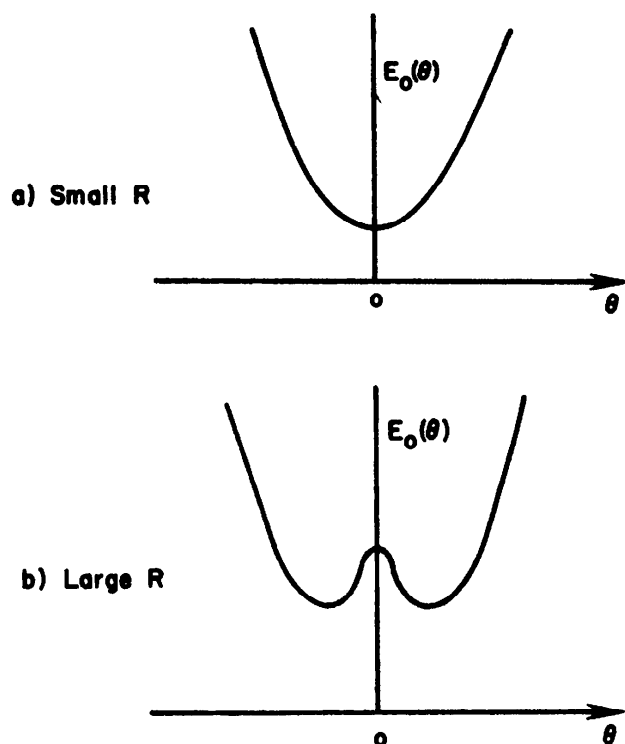


Figure 3.17 Qualitative behavior of the unrestricted energy of H_2 as a function of θ for small and large internuclear distances: a) small R ; b) large R .

$E_0''(0)$ and η as a function of bond length. At short bond lengths $E_0''(0) > 0$ and $\eta > 1$. As the bond length increases both $E_0''(0)$ and η decrease monotonically, until they reach a limit at $R = \infty$ of $E_0''(0) = -1/2 (\phi_1\phi_1 | \phi_1\phi_1)$ and $\eta = 1/2$. At a transition point, which occurs in the vicinity of $R = 2.3$ a.u., the second derivative $E_0''(0)$ becomes negative and simultaneously η becomes less than 1. The behavior of the solutions is therefore as follows: At short bond lengths $\eta > 1$, the restricted solution is a true minimum, and no unrestricted solution exists. On increasing the bond length the value of η decreases until, at a distance of approximately 2.3 a.u., η becomes 1 and a saddle point occurs in the energy. This transition point defines the onset of an unrestricted solution. At a bond length beyond this, the restricted solution ($\theta = 0$) is actually a maximum in the energy as shown in Fig. 3.17. When an unrestricted solution exists ($\eta \leq 1$), the value of η can be equated to $\cos^2 \theta$. As the bond length becomes larger and larger, θ gives to the limit of 45° appropriate to isolated hydrogen atoms. A potential curve for STO-3G H_2 showing the two solutions is shown in Fig. 3.18. The unrestricted energy goes smoothly to the limit of two hydrogen atoms calculated with the same basis set, i.e., $2(\phi_1 | h | \phi_1)$. The restricted energy goes to a limit $1/2(\phi_1\phi_1 | \phi_1\phi_1)$ above the right result. Also shown in Fig. 3.18 is the essentially exact result of Kolos and Wolniewicz.⁵ The hydrogen atom energies used in the figure (-0.4666 and -0.5) are obtained with the basis sets employed in the respective methods. Thus, both curves go to zero at large R . The corresponding curves for a 6-31G** basis set are shown in Fig. 3.19.

The "correct" dissociation of H_2 , which we have obtained by using an unrestricted wave function, is not free of faults. The unrestricted wave

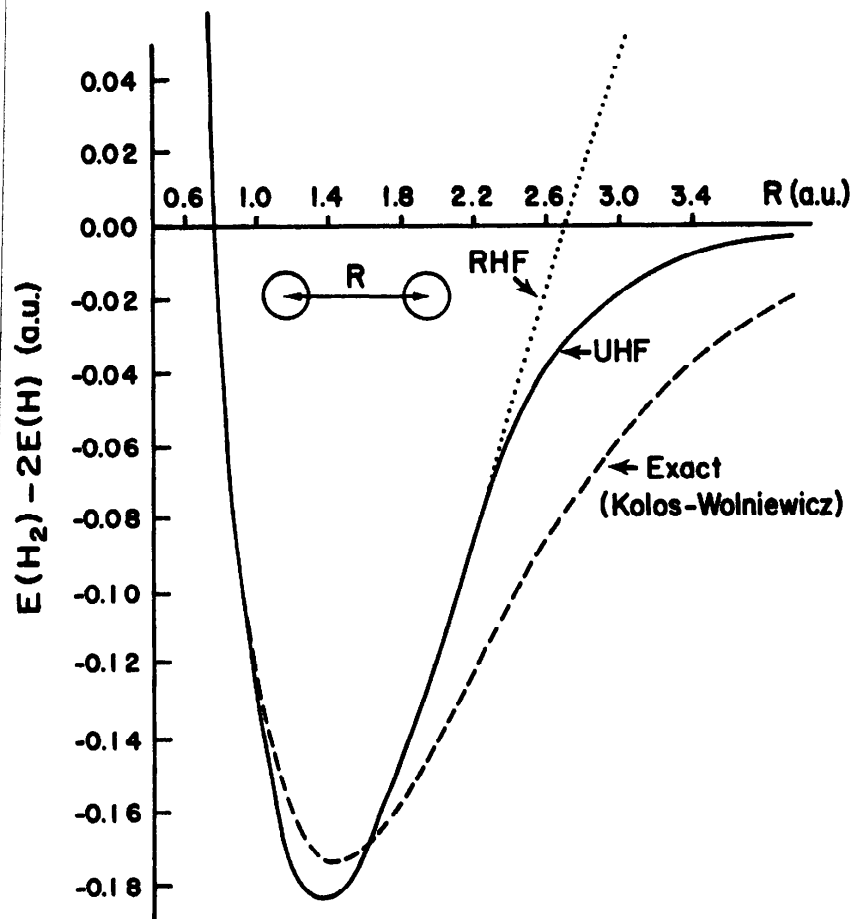


Figure 3.18 STO-3G potential curves for H_2 .

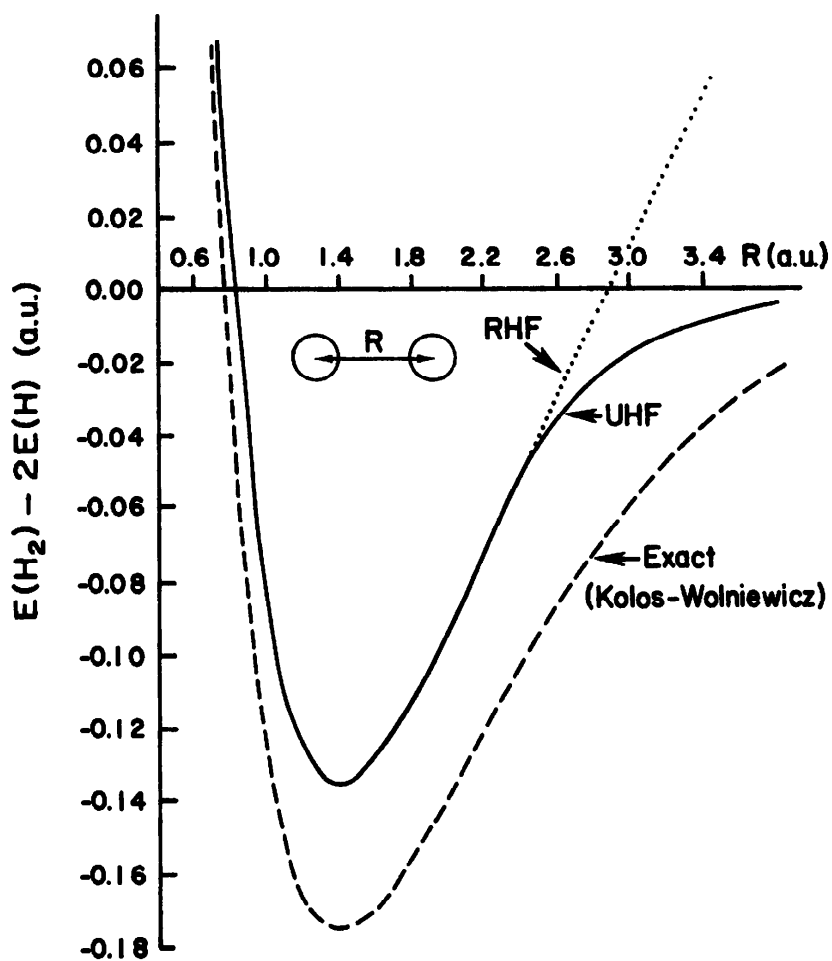


Figure 3.19 6-31G** potential energy curves for H_2 .

function is not a pure singlet as one would like it to be. The energy goes to the correct limit but the total wave function does not, as we shall now see. In the limit $R \rightarrow \infty$, the molecular orbitals become $\psi_1^\alpha = \phi_1$ and $\psi_1^\beta = \phi_2$ and the unrestricted single determinant $|\Psi_0\rangle$ of Eq. (3.367) becomes

$$\lim_{R \rightarrow \infty} |\Psi_0\rangle = |\phi_1(1)\bar{\phi}_2(2)\rangle \quad (3.379)$$

This, however, is not the correct form for a singlet wave function in which electrons occupy different spatial orbitals ϕ_1 and ϕ_2 . In analogy to Eq. (2.260), the singlet wave function should be

$$\lim_{R \rightarrow \infty} |\Phi_0\rangle = 2^{-1/2} [|\phi_1(1)\bar{\phi}_2(2)\rangle + |\phi_2(1)\bar{\phi}_1(2)\rangle] \quad (3.380)$$

The orbitals are correct but the total wave function is not. An alternative way of looking at this problem is obtained by substituting the expansions (3.358) and (3.359) for the unrestricted molecular orbitals into the single determinant $|\Psi_0\rangle$ and expanding the determinant

$$\begin{aligned} |\Psi_0\rangle &= |\psi_1^\alpha \bar{\psi}_1^\beta\rangle = \cos^2 \theta |\psi_1 \bar{\psi}_1\rangle - \sin^2 \theta |\psi_2 \bar{\psi}_2\rangle \\ &\quad - (2)^{1/2} \cos \theta \sin \theta [|\psi_1 \bar{\psi}_2\rangle - |\psi_2 \bar{\psi}_1\rangle] / (2)^{1/2} \\ &= \cos^2 \theta |\psi_1 \bar{\psi}_1\rangle - \sin^2 \theta |\psi_2 \bar{\psi}_2\rangle \\ &\quad - (2)^{1/2} \cos \theta \sin \theta |{}^3\Psi_1^2\rangle \end{aligned} \quad (3.381)$$

Here, $|{}^3\Psi_1^2\rangle$ is the singly excited triplet configuration defined in Eq. (2.261). The closed-shell determinants $|\psi_1 \bar{\psi}_1\rangle$ and $|\psi_2 \bar{\psi}_2\rangle$ are, of course, singlets. An unrestricted single determinant for the ground state of H_2 is thus not a pure singlet but is contaminated by a triplet. The mixing of the doubly excited determinant $|\psi_2 \bar{\psi}_2\rangle$ with $|\psi_1 \bar{\psi}_1\rangle$ allows the dissociation to go to the correct limit, but the triplet contaminant is required if the final wave function is to be a single determinant. As $R \rightarrow \infty$ the triplet contamination increases until it represents 50% of the wave function,

$$\lim_{R \rightarrow \infty} |\Psi_0\rangle = 1/2 [|\psi_1 \bar{\psi}_1\rangle - |\psi_2 \bar{\psi}_2\rangle - (2)^{1/2} |{}^3\Psi_1^2\rangle] \quad (3.382)$$

Although the correct dissociation energy is obtained using an unrestricted wave function, the poor wave function will limit the desirability of using, near the dissociation limit, an unrestricted single determinant as a starting point for configuration interaction or perturbation calculations.

Exercise 3.44 Derive Eq. (3.379) from Eq. (3.382).

We have only discussed the restricted Hartree-Fock dissociation problem for the minimal basis model of H_2 . The ideas presented are not limited to H_2 , however, and very similar effects will occur for other closed-shell systems when a bond is stretched. In H_2 , the onset of unrestricted solutions

occurs beyond the equilibrium distance but in the general case there may even be unrestricted solutions at the experimental geometry. By an extension of our analysis, it is possible to derive general conditions under which there exists an unrestricted solution lower in energy than the closed-shell restricted solution (Thouless, 1961).

NOTES

1. J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, H. B. Schlegel, D. J. Defrees, and J. A. Pople, *Gaussian 80*, program #406, Quantum Chemistry Program Exchange, Indiana University. More recent versions, such as *Gaussian 88*, are available via Professor John Pople of Carnegie-Mellon University.
2. Hartree-Fock theory in special cases, such as for restricted open-shell wave functions, involves a multideterminantal wave function. Since we will be concerned only with unrestricted open-shell wave functions, all Hartree-Fock wave functions will be single determinants.
3. In principle it is possible to use the procedures to be discussed in this section to obtain restricted closed-shell excited states, but there is no general way of keeping such calculations from converging to the ground state $|\Psi_0\rangle$ if the excited state has the same symmetry as the ground state.
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8. S. Huzinaga, Gaussian-type functions for polyatomic systems. I, *J. Chem. Phys.* **42**: 1293 (1965).
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10. The slash here separates heavy atom (Li-Ne) basis functions from hydrogen atom basis functions.
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FURTHER READING

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- England, W., Salmon, L. S., and Ruedenberg, K., Localized MO's: A bridge between chemical intuition and molecular quantum mechanics, in *Topics in Current Chemistry*, Springer-Verlag, 1971; Caldwell, D. and Eyring, H., Localized orbitals in spectroscopy, *Adv. Quantum Chem.* **11**: 93 (1978). These two references discuss the invariance of Hartree-Fock orbitals to a unitary transformation, and the physical interpretation of particular