

Spectrum Prediction; Spectrum Simulation

See *Infrared Data Correlations with Chemical Structure; Infrared Spectra Interpretation by the Characteristic Frequency Approach; NMR Data Correlation with Chemical Structure; Spectroscopic Databases; and Structure Determination by Computer-based Spectrum Interpretation.*

Spherical Harmonic

A wavefunction $Y_{l,m}$ for a specific state of orbital angular momentum, i.e., orthogonal functions of the angular coordinates which satisfy the differential equation $\Lambda^2 Y = -l(l+1)Y$, where Λ^2 is the Legendre operator. The functions are polynomials in $\sin \theta$ and $\cos \theta$. Spherical harmonics are the angular factors in centrosymmetric atomic orbitals.

Spin Contamination

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Abbreviations

AUMP n = annihilated unrestricted n th-order Møller-Plesset; AUHF = annihilated unrestricted Hartree-Fock; BD = Brueckner doubles; CCD = coupled cluster doubles; CCSD = coupled cluster singles and doubles; CID = configuration interaction doubles; CISD = configuration interaction singles and doubles; EHF = extended Hartree-Fock; HPHF = half-projected Hartree-Fock; MP2 = second-order Møller-Plesset perturbation; MP n = n th-order Møller-Plesset perturbation; MRDCI = multireference determinant configuration interaction; PMP n = projected MP n ; PUHF = projected unrestricted Hartree-Fock; QCISD = quadratic configuration interaction singles and doubles; RMP2 = restricted second-order Møller-Plesset perturbation; ROMP n = n th-order restricted open-shell Møller-Plesset perturbation; SUHF = spin-constrained Hartree-Fock; SUMP n = spin-constrained MP n ; UMP2 = unrestricted second-order Møller-Plesset perturbation; UMP n = unrestricted MP n ; UQCI = unrestricted quadratic configuration interaction.

1 INTRODUCTION

Solutions of the nonrelativistic Schrödinger equation for electronic systems are eigenfunctions of the total spin; in particular, they are eigenfunctions of the \hat{S}_z and \hat{S}^2 operators. For closed shell systems, where $\langle \hat{S}^2 \rangle = 0$, it is easy to construct simple approximations such as spin restricted Hartree-Fock (RHF) wavefunctions that are eigenfunctions of \hat{S}^2 by requiring the orbitals to be doubly occupied (one α and one β -electron). For open-shell systems, spin restricted open-shell Hartree-Fock (ROHF) wavefunctions are also eigenfunctions of \hat{S}^2 , and have unpaired electrons in α orbitals and the remaining electrons in doubly occupied orbitals. An alternative single determinantal wavefunction for open-shell systems is spin unrestricted Hartree-Fock (UHF), which has different spatial orbitals for α and β electrons. Although UHF wavefunctions are not eigenfunctions of \hat{S}^2 , they have some advantages over ROHF for open-shell systems in that they yield acceptable energies, structures, and spin densities in a single determinantal formalism. They are also a better starting point for exploring potential energy surfaces, since UHF methods are better able to represent bond dissociations than ROHF calculations. Furthermore, corrections for electron correlation are simpler in the UHF formalism.

A major shortcoming of methods based on spin-unrestricted determinants is that the wavefunctions are not eigenfunctions of \hat{S}^2 . If these wavefunctions are expanded in terms of pure spin wavefunctions, they consist of the desired spin state and contamination from higher spin states. Usually the spin contamination is small; however, if the contamination is large, the shape of the potential energy surface can be distorted by contributions from unwanted spin states. It can also cause methods such as Møller-Plesset perturbation theory to converge very slowly.¹ Such situations occur when occupied and unoccupied orbitals become nearly degenerate in an RHF treatment. For example, when a single bond is stretched toward breaking, or when a π bond is twisted to a perpendicular conformation, the ground state UHF wavefunction has a large contamination from the triplet. Similarly, radicals with extensive delocalization of the odd electron can have sizable contamination from quartet spin states. In general, transition states are more susceptible to spin contamination than equilibrium structures, since they are more likely to have elongated bonds, twisted π systems, or delocalized unpaired electrons. Spin projection methods were reviewed a number of years ago.² This article deals with projection methods for treating spin contamination in unrestricted calculations.

Modest spin contamination can often be handled by projection methods after the wavefunction has been determined. This improves the behavior of some calculations, such as unrestricted Møller-Plesset perturbation theory, but degrades other methods such as UHF and density functional methods. Severe spin contamination in a wavefunction based on a UHF determinant indicates that a single reference determinant calculation is inadequate. Multi-configuration self-consistent field (MCSCF) calculations with spin-adapted configurations are more appropriate for these situations. Dynamic correlation can be added using multireference determinant configuration interaction (MRDCI) with spin-adapted configurations.

Bond dissociation curves provide a more convenient system for illustrating the problems of spin contamination than

calculations of radicals, since the magnitude of the effect can be easily varied by changing the bond length, and the approximate calculations can be readily compared to accurate potentials. However, the primary purpose of the spin projection methods discussed in this article is not necessarily to compute accurate dissociation potentials. For small molecules, this is better done using MCSCF and MRDCI methods. Spin projection is particularly useful for larger open-shell systems that need to be treated by methods based on UHF reference determinants, including radicals, diradicals, and some transition states.

2 A SIMPLE EXAMPLE: DISSOCIATION OF THE HYDROGEN MOLECULE

The problems associated with spin contamination in UHF wavefunctions are easily illustrated by considering a minimal basis set calculation of H_2 . If χ_a and χ_b are the basis functions on H_a and H_b , respectively, the σ and σ^* spin orbitals are given by

$$\begin{aligned}\phi_{\sigma}^{\text{RHF}} &= N_{\sigma}(\chi_a + \chi_b)\alpha \\ \bar{\phi}_{\sigma}^{\text{RHF}} &= N_{\sigma}(\chi_a + \chi_b)\beta \\ \phi_{\sigma^*}^{\text{RHF}} &= N_{\sigma^*}(\chi_a - \chi_b)\alpha \\ \bar{\phi}_{\sigma^*}^{\text{RHF}} &= N_{\sigma^*}(\chi_a - \chi_b)\beta\end{aligned}\quad (1)$$

where N_{σ} and N_{σ^*} are the normalization constants. These orbitals can be used to construct wavefunctions for the singlet ground state, singly excited state, and doubly excited state, and for the $s_z = 0$ component of the triplet state:

$$\begin{aligned}{}^1\Psi_0^{\text{RHF}} &= |\phi_{\sigma}^{\text{RHF}}\bar{\phi}_{\sigma}^{\text{RHF}}| \\ {}^1\Psi_1^{\text{RHF}} &= 1/\sqrt{2} |\phi_{\sigma}^{\text{RHF}}\bar{\phi}_{\sigma^*}^{\text{RHF}}| + |\phi_{\sigma^*}^{\text{RHF}}\bar{\phi}_{\sigma}^{\text{RHF}}| \\ {}^1\Psi_2^{\text{RHF}} &= |\phi_{\sigma^*}^{\text{RHF}}\bar{\phi}_{\sigma^*}^{\text{RHF}}| \\ {}^3\Psi^{\text{RHF}} &= 1/\sqrt{2} |\phi_{\sigma}^{\text{RHF}}\bar{\phi}_{\sigma^*}^{\text{RHF}}| - |\phi_{\sigma^*}^{\text{RHF}}\bar{\phi}_{\sigma}^{\text{RHF}}|\end{aligned}\quad (2)$$

In a UHF wavefunction, the α and β orbitals have different spatial parts. The UHF spin orbitals can be expressed as linear combinations of the RHF orbitals:

$$\begin{aligned}\phi_{\sigma}^{\text{UHF}} &= \cos\theta\phi_{\sigma}^{\text{RHF}} + \sin\theta\phi_{\sigma^*}^{\text{RHF}} \\ \bar{\phi}_{\sigma}^{\text{UHF}} &= \cos\theta\bar{\phi}_{\sigma}^{\text{RHF}} - \sin\theta\bar{\phi}_{\sigma^*}^{\text{RHF}}\end{aligned}\quad (3)$$

The ground state UHF wavefunction can be expressed in terms of the RHF wavefunctions by expanding the determinant in RHF orbitals:

$$\begin{aligned}\Psi_0^{\text{UHF}} &= |\phi_{\sigma}^{\text{UHF}}\bar{\phi}_{\sigma}^{\text{UHF}}| = |(\cos\theta\phi_{\sigma}^{\text{RHF}} + \sin\theta\phi_{\sigma^*}^{\text{RHF}}) \\ &\quad \times (\cos\theta\bar{\phi}_{\sigma}^{\text{RHF}} - \sin\theta\bar{\phi}_{\sigma^*}^{\text{RHF}})| \\ &= \cos^2\theta|\phi_{\sigma}^{\text{RHF}}\bar{\phi}_{\sigma}^{\text{RHF}}| - \sin^2\theta|\phi_{\sigma^*}^{\text{RHF}}\bar{\phi}_{\sigma^*}^{\text{RHF}}| \\ &\quad - \cos\theta\sin\theta(|\phi_{\sigma}^{\text{RHF}}\bar{\phi}_{\sigma^*}^{\text{RHF}}| - |\phi_{\sigma^*}^{\text{RHF}}\bar{\phi}_{\sigma}^{\text{RHF}}|) \\ &= \cos^2\theta{}^1\Psi_0^{\text{RHF}} - \sin^2\theta{}^1\Psi_2^{\text{RHF}} - 1/\sqrt{2}\sin 2\theta{}^3\Psi^{\text{RHF}}\end{aligned}\quad (4)$$

The eigenvalue of \hat{S}^2 is $s(s+1)$ where s is the total spin (e.g., 0 for a singlet and 2 for a triplet). Thus, the deviation of S^2

from $s(s+1)$ is a direct measure of the contamination from higher spin states.

Figure 1 shows the bond dissociation potential for a minimal basis set calculation of H_2 . At intermediate bond lengths (e.g., twice equilibrium), the UHF wavefunction is more stable than the RHF solution. The doubly excited configuration ${}^1\Psi_2^{\text{RHF}}$ provides some electron correlation and lowers the energy, while the triplet configuration ${}^3\Psi^{\text{RHF}}$ raises the energy. The optimum mixture of these two effects is determined by the SCF procedure. At short bond lengths, the triplet configuration is too high in energy, and no mixing occurs, i.e., $\theta = 0$, and the wavefunction is RHF. At large distances, ${}^3\Psi^{\text{RHF}}$ and ${}^1\Psi_0^{\text{RHF}}$ are almost degenerate, and the UHF wavefunction contains nearly equal parts of singlet and triplet. The α spin orbital is localized on one atom and the β orbital is localized on the other ($\Psi_0^{\text{UHF}} \approx |\chi_a\alpha\chi_b\beta|$ as $\theta \rightarrow 45^\circ$), allowing dissociation into two H atoms. By contrast, the RHF ground state dissociates to a much higher limit that is a mixture of $H + H$ and $H^+ + H^-$ (${}^1\Psi_0^{\text{RHF}} = |N(\chi_a + \chi_b)\alpha N(\chi_a + \chi_b)\beta| = N^2(|\chi_a\alpha\chi_b\beta| + |\chi_b\alpha\chi_a\beta| + |\chi_a\alpha\chi_a\beta| + |\chi_b\alpha\chi_b\beta|)$). In the intermediate region, the most stable wavefunction changes from RHF to UHF (see *Instability of the Hartree-Fock Solution*). The energy, the first derivative of the energy, and the expectation value of \hat{S}^2 are continuous at this point, but the derivative of $\langle \hat{S}^2 \rangle$ is not.

The H_2 dissociation potential in Figure 1 shows the behavior of a number of levels of theory. Projection methods

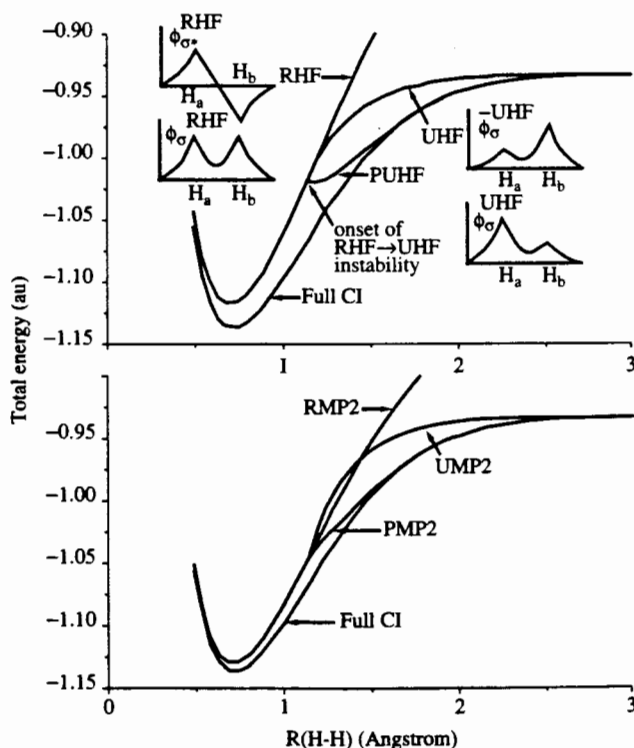


Figure 1 Bond dissociation potential for H_2 computed with RHF, UHF, PUHF (projected UHF), RMP2 (restricted MP2), UMP2 (unrestricted MP2), PMP2 (projected MP2), and full configuration interaction levels of theories using a minimal basis set. Typical RHF and UHF orbitals are shown in the insets; the UHF bonding orbitals can be written as a linear combination of the RHF bonding and antibonding orbitals (equation 3) (adapted with the permission from Ref. 12)

(see below) can be used to remove spin contamination after the UHF wavefunction has been determined; however, this destroys the balance between the energy-lowering (correlating) effect of ${}^1\Psi_2^{\text{RHF}}$ and the energy-raising effect of ${}^3\Psi^{\text{RHF}}$. When ${}^3\Psi^{\text{RHF}}$ is removed, the PUHF curve is too low, showing a cusp and a minimum near the onset of the RHF \rightarrow UHF instability. On the other hand, if correlation corrections are added by perturbation theory (see *Møller-Plesset Perturbation Theory*), e.g., second order Møller-Plesset perturbation theory (MP2), the spin restricted calculation (RMP2) goes toward $-\infty$ at very long bond lengths because the energy difference in the denominator approaches zero, but the unrestricted calculation (UMP2) approaches the right limit. However, there is a distinct hump in the potential beyond the RHF \rightarrow UHF instability. Although MP2 takes care of a large portion of the electron correlation correction, it cannot readily remove higher spin states. Thus significant spin contamination leads to extremely slow convergence with increasing orders of perturbation theory for such systems.¹ Spin projection, however, removes the contamination and yields a curve that is comparable to the full configuration interaction calculation at intermediate and long bond distances. The purpose of the projection methods discussed in this chapter is to correct the behavior of spin-unrestricted perturbation methods in regions of modest contamination.

3 EVALUATION OF SPIN OPERATORS

The \hat{S}^2 operator can be expressed in terms of the z component of the total spin and the raising and lowering operators:

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \hat{S}_z^2 + \hat{S}_+ \hat{S}_- + \hat{S}_- \hat{S}_+ \quad (5)$$

In terms of the operators for the individual electrons, \hat{S}^2 is

$$\begin{aligned} \hat{S}^2 = & \left(\sum_i \hat{s}_z(i) \right) \left(\sum_j \hat{s}_z(j) \right) + \sum_i \hat{s}_z(i) \\ & + \sum_i \hat{s}_-(i) \hat{s}_+(i) + \sum_{i \neq j} \hat{s}_-(i) \hat{s}_+(j) \end{aligned} \quad (6)$$

where i and j run over the electrons. For the Hartree-Fock wavefunction, the orbitals are eigenfunctions of \hat{s}_z but not of \hat{s}_\pm :

$$\begin{aligned} \hat{s}_z \phi_i &= \frac{1}{2} \phi_i & \hat{s}_z \bar{\phi}_j &= -\frac{1}{2} \bar{\phi}_j \\ \hat{s}_+ \phi_i &= 0 & \hat{s}_+ \bar{\phi}_j &= \sum_i S_{ij} \phi_i \\ \hat{s}_- \phi_i &= \sum_{\bar{j}} S_{i\bar{j}} \bar{\phi}_{\bar{j}} & \hat{s}_- \bar{\phi}_j &= 0 \end{aligned} \quad (7)$$

where a bar over the orbital or index indicates a β electron and no bar indicates an α electron. The α - β overlap matrix, $S_{i\bar{j}}$, is the overlap between the spatial parts of the α and β orbitals:

$$S_{i\bar{j}} = \int \phi_i^* \bar{\phi}_j d\tau \quad (8)$$

A Hartree-Fock wavefunction is an eigenfunction of \hat{S}_z :

$$\hat{S}_z \Psi_0 = s_z \Psi_0 \quad s_z = (n_\alpha - n_\beta)/2 \quad (9)$$

where n_α and n_β are the number of α and β electrons, respectively. The expectation value of \hat{S}^2 for a Hartree-Fock wavefunction is

$$\langle \hat{S}^2 \rangle_0 = \langle \Psi_0 | \hat{S}^2 | \Psi_0 \rangle = s_z^2 + s_z + n_\beta - \sum_{i\bar{j}} (S_{i\bar{j}})^2 \quad (10)$$

The first two terms follow directly from the first two terms in equation (6), since the Hartree-Fock orbitals are eigenfunctions of \hat{s}_z . The third term sums to n_β since $\int \phi_i^* \hat{s}_+ \phi_i d\tau = 0$ for α orbitals and $\int \bar{\phi}_j^* \hat{s}_- \bar{\phi}_j d\tau = 1$ for β orbitals. The fourth term involves the α - β overlap with the negative sign arising from the antisymmetry of the Hartree-Fock wavefunction. Note that for RHF, the spatial parts of corresponding α and β orbitals are the same; thus $S_{i\bar{j}}$ is a unit matrix and $\langle \hat{S}^2 \rangle_0$ evaluates to $s_z^2 + |s_z|$ for an ROHF determinant.

The matrix elements for \hat{S}^{2n} needed for the spin projection methods discussed below involve multiple products of the α - β overlap matrix and can be computed readily for UHF wavefunctions.³ Since the Hartree-Fock energy is invariant to unitary transformations among occupied orbitals of the same spin, the α and β orbitals can be rotated so that the α - β overlap matrix is diagonal. These are termed corresponding orbitals,³ and their use greatly simplifies expressions for matrix elements of \hat{S}^{2n} .

For second-order many body or Møller-Plesset perturbation theory (MBPT2 or MP2; see *Møller-Plesset Perturbation Theory*), the first-order wavefunction, Ψ_1 , can be written as

$$\Psi_1 = \sum_{i < j} \sum_{a < b} a_{ij}^{ab} \Psi_{ij}^{ab} \quad (11)$$

where Ψ_{ij}^{ab} is a doubly excited determinant, in which occupied spin orbitals i and j have been replaced by virtual spin orbitals a and b ; a_{ij}^{ab} is the corresponding amplitude. For an MP2 calculation, the expectation value of \hat{S}^2 correct to first order is

$$\begin{aligned} \langle \hat{S}^2 \rangle &= \langle \Psi_0 | \hat{S}^2 | \Psi_0 \rangle + 2 \langle \Psi_0 | \hat{S}^2 | \Psi_1 \rangle \\ &= \langle \hat{S}^2 \rangle_0 + 2 \sum_{i\bar{j}ab} a_{i\bar{j}}^{ab} \langle \Psi_0 | \hat{S}^2 | \Psi_{i\bar{j}}^{ab} \rangle \end{aligned}$$

$$\langle \Psi_0 | \hat{S}^2 | \Psi_{i\bar{j}}^{ab} \rangle = -S_{a\bar{j}} S_{i\bar{b}} \quad (12)$$

where the sum is over all occupied α orbitals, i , occupied β orbitals, \bar{j} , virtual α orbitals, a , and virtual β orbitals, \bar{b} . Expressions for $\langle \hat{S}^2 \rangle$ for higher orders of perturbation theory become progressively more complicated.⁴

For correlated methods such as truncated configuration interaction (CID or CISD), coupled cluster (CCD or CCSD), quadratic configuration interaction (QCISD) and Brueckner doubles (BD) (see *Configuration Interaction* and *Coupled-cluster Theory*), the energy and wavefunction can be written as

$$E = \langle \Psi_0 | \hat{H} | \Psi \rangle, \quad \Psi = \Psi_0 + \sum_{ia} a_i^a \Psi_i^a + \sum_{i < j} \sum_{a < b} a_{ij}^{ab} \Psi_{ij}^{ab} + \dots \quad (13)$$

To compute S^2 for correlated methods, a perturbation $\lambda \hat{S}^2$ can be added to the Hamiltonian, and \hat{S}^2 evaluated as a derivative:⁵

$$\langle \hat{S}^2 \rangle = dE/d\lambda|_{\lambda=0} = \langle \Psi_0 | \hat{S}^2 | \Psi \rangle + \langle \Psi_0 | \hat{H} | d\Psi/d\lambda \rangle \quad (14)$$

The first term is the Hellmann-Feynman term, and can be evaluated readily:

$$\langle \Psi_0 | \hat{S}^2 | \Psi \rangle = \langle \Psi_0 | \hat{S}^2 | \Psi_0 \rangle + \sum_{ia} a_i^a \langle \Psi_0 | \hat{S}^2 | \Psi_i^a \rangle + \sum_{\bar{j}\bar{b}} a_{\bar{j}}^{\bar{b}} \langle \Psi_0 | \hat{S}^2 | \Psi_{\bar{j}}^{\bar{b}} \rangle + \sum_{i\bar{j} > a\bar{b}} a_{i\bar{j}}^{a\bar{b}} \langle \Psi_0 | \hat{S}^2 | \Psi_{i\bar{j}}^{a\bar{b}} \rangle \quad (15)$$

$$\langle \Psi_0 | \hat{S}^2 | \Psi_i^a \rangle = - \sum_{\bar{j}} S_{a\bar{j}} S_{i\bar{j}} \langle \Psi_0 | \hat{S}^2 | \Psi_{\bar{j}}^{\bar{b}} \rangle = - \sum_{\bar{i}} S_{i\bar{j}} S_{i\bar{i}} \quad (16)$$

where i and a are occupied and virtual α spin orbitals, and \bar{j} and \bar{b} are occupied and virtual β spin orbitals. Excitations higher than doubles (including perturbative corrections for triples) do not contribute to $\langle \Psi_0 | \hat{S}^2 | \Psi \rangle$ since \hat{S}^2 is a two-electron operator (however, they do contribute to matrix elements involving \hat{S}^4 , \hat{S}^6 , etc., that arise in projection operators). The second term in equation (14) involves the derivative of the wavefunction, and appears to be small for $\langle \hat{S}^2 \rangle$. It can be evaluated by perturbation theory or by coupled perturbed methods.^{4,6}

The calculation of S^2 for density functional methods (see *Density Functional Theory (DFT), Hartree-Fock (HF), and the Self-consistent Field*) is somewhat problematic because these methods do not utilize wavefunctions.⁷ In the non-interacting system, a DFT wavefunction can be constructed as a Slater determinant of Kohn-Sham orbitals, and S^2 can be calculated by equation (10). For the interacting system, S^2 can be computed from the two-particle density, which can be written in terms of one-particle densities and hole functions.⁷ Examples given by Becke and co-workers⁷ indicate that the values for S^2 for the interacting system may be slightly larger than for the non-interacting system, which are in turn larger than the exact values.

Figure 2 shows the behavior of S^2 for various levels of theory as a function of the bond length in hydrogen fluoride.⁴ For SCF, MP n , CI, and CCD methods, S^2 rises rapidly as the bond is stretched beyond the RHF \rightarrow UHF instability (near 1.3 Å). For QCISD and CCSD, S^2 increases more slowly, indicating they are better able to handle modest levels of

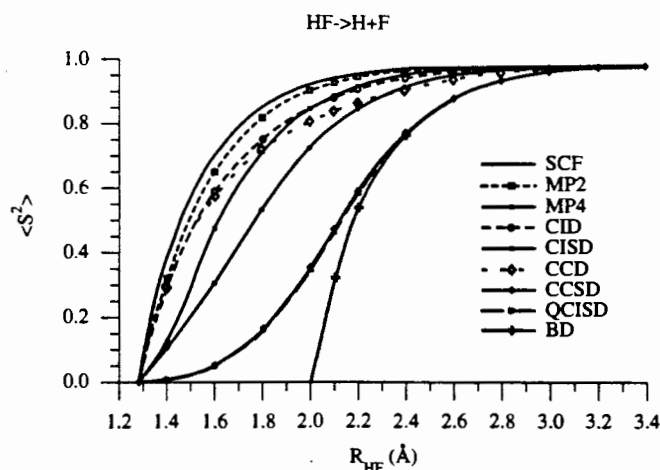


Figure 2 Values of S^2 as a function of bond length for the dissociation of hydrogen fluoride, computed at various levels of theory with the 6-31G basis set (reproduced with permission from Ref. 4)

spin contamination. For BD, the switch from spin restricted to unrestricted occurs at greater bond elongation than for methods based on Hartree-Fock reference determinants. Beyond the RBD \rightarrow UBD instability (near 2.0 Å), S^2 for QCI, CC, and BD rapidly approaches the asymptotic value of 1 (equal mixtures of singlet and triplet). Spin contamination in radicals is also much lower for QCI, CC, BD, and DFT methods than for spin unrestricted HF, MP n , and CI.^{8,9}

4 PROJECTION OPERATORS

An approximate wavefunction may be a mixture of different spin states. Unwanted spin states can be removed with annihilation and projection operators.¹⁰ The annihilation operator that removes the state with spin k is

$$\hat{A}_k = [\hat{S}^2 - k(k+1)] / [(\hat{S}^2) - k(k+1)] \quad (17)$$

Note that in addition to removing all components of the wavefunction with spin k , the annihilation operator changes the relative weighting of the remaining components. A projection operator to remove all spin contamination can be constructed in a similar manner:¹⁰

$$\hat{P}_s = \prod_{k \neq s} \frac{\hat{S}^2 - k(k+1)}{s(s+1) - k(k+1)} \quad (18)$$

Note that the projection operator is idempotent, $\hat{P}_s^2 = \hat{P}_s$, but an annihilation operator generally is not; both the annihilation and the projection operators commute with the nonrelativistic Schrödinger Hamiltonian. In practice, the contamination may come from only a few spin states, and the projector can be approximated by the product of a few annihilators, typically one or two annihilators for each unpaired electron, or each electron pair being disrupted. A projection operator that removes spins $s+1$ to $s+n$ involves operators \hat{S}^{2n} through \hat{S}^{2n} .

5 PROJECTED ENERGIES

If the projection operator is applied after the wavefunction has been determined, the expectation value of the energy can be written as

$$E_{\text{proj}} = (\hat{P}_s \Psi | \hat{H} | \hat{P}_s \Psi) / (\hat{P}_s \Psi | \hat{P}_s \Psi) = \langle \Psi | \hat{H} \hat{P}_s | \Psi \rangle / \langle \Psi | \hat{P}_s | \Psi \rangle \quad (19)$$

by taking advantage of the fact the \hat{P}_s is idempotent and commutes with the Hamiltonian. For Hartree-Fock theory, this expression can be simplified by inserting the identity $\hat{I} = \sum |\psi_i\rangle \langle \psi_i|$ and noting that $\langle \Psi_0 | \hat{H} | \psi_i \rangle$ is nonzero only when ψ_i is the ground state or a doubly excited configuration:

$$\begin{aligned} E_{\text{PUHF}} &= \sum_i \frac{\langle \Psi_0 | \hat{H} | \psi_i \rangle \langle \psi_i | \hat{P}_s | \Psi_0 \rangle}{\langle \Psi_0 | \hat{P}_s | \Psi_0 \rangle} \\ &= \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \sum_{i < j} \sum_{a < b} \frac{\langle \Psi_0 | \hat{H} | \Psi_{ij}^{ab} \rangle \langle \Psi_{ij}^{ab} | \hat{P}_s | \Psi_0 \rangle}{\langle \Psi_0 | \hat{P}_s | \Psi_0 \rangle} \\ &= \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \langle \Psi_0 | \hat{H} | \tilde{\Psi} \rangle = E_{\text{UHF}} + \Delta E_{\text{PUHF}} \quad (20) \end{aligned}$$

where the correction to the Hartree-Fock wavefunction arising from the spin projection is

$$\tilde{\Psi} = \sum_{i < j} \frac{\Psi_{ij}^{ab} \langle \Psi_{ij}^{ab} | \hat{P}_s | \Psi_0 \rangle}{\langle \Psi_0 | \hat{P}_s | \Psi_0 \rangle} \quad (21)$$

The projection converges rapidly with respect to the number of spins, and the product in equation (19) can often be limited to the lowest few spins, i.e., the projector can be replaced by the product of one or two annihilators. However, if significant contamination from higher spin states remains, the partially projected energy can be lower than the fully projected energy.¹¹ Because of the problematic behavior of PUHF bond dissociation curves, such as shown in Figure 1, PUHF energies are not recommended for exploring potential energy surfaces or calculating energy differences.

For MPn the energy can be written as $E_{MPn} = \langle \Psi_0 | \hat{H} | \Psi_0 + \Psi_1 \cdots \Psi_{n-1} \rangle$, and by analogy to equation (21) the projected energy can be estimated using^{4,12}

$$E_{\text{proj MPn}} = \frac{\langle \Psi_0 | \hat{H} \hat{P}_s | \Psi_0 + \Psi_1 \cdots \Psi_{n-1} \rangle}{\langle \Psi_0 | \hat{P}_s | \Psi_0 + \Psi_1 \cdots \Psi_{n-1} \rangle} \\ = \langle \Psi_0 | \hat{H} | \Psi_0 + \Psi_1 \cdots \Psi_{n-1} \rangle \\ + \sum_{i < j} \frac{\langle \Psi_0 | \hat{H} | \Psi_{ij}^{ab} \rangle \langle \Psi_{ij}^{ab} | \hat{P}_s | \Psi_0 + \Psi_1 \cdots \Psi_{n-1} \rangle}{\langle \Psi_0 | \hat{P}_s | \Psi_0 + \Psi_1 \cdots \Psi_{n-1} \rangle} \quad (22)$$

Alternatively, the projection operator can be applied during the development of the perturbation series, leading to the following estimate:¹³

$$E_{\text{proj MPn}} = E_{\text{PUHF}} + \sum_{k=2}^n \tilde{E}_k \quad (23) \\ \tilde{E}_k = (\langle \Psi_0 | \hat{H} \hat{P}_s | \Psi_{k-1} \rangle - E_0 \langle \Psi_0 | \hat{P}_s | \Psi_{k-1} \rangle) \\ - \sum_{r=1}^{k-1} \tilde{E}_r \langle \Psi_0 | \hat{P}_s | \Psi_{k-r} \rangle / \langle \Psi_0 | \hat{P}_s | \Psi_0 \rangle$$

The same expression is obtained if equation (22) is expanded to the appropriate order.

A simple, approximate formula for projected MPn energies can be obtained by Schmidt orthogonalization of the perturbative correction for electron correlation, $\Psi_1 + \cdots + \Psi_{n-1}$, to the contribution from spin projection calculated at the Hartree-Fock level, $\tilde{\Psi}$:¹²

$$\tilde{\Psi}_n = \Psi_n - \tilde{\Psi} \langle \Psi_n | \tilde{\Psi} \rangle / \langle \tilde{\Psi} | \tilde{\Psi} \rangle \quad (24) \\ E_{\text{PMPn}} = \langle \Psi_0 | \hat{H} | \Psi_0 + \tilde{\Psi} + \tilde{\Psi}_1 + \cdots + \Psi_{n-1} \rangle \\ = \langle \Psi_0 | \hat{H} | \Psi_0 + \Psi_1 + \cdots + \Psi_{n-1} \rangle + \langle \Psi_0 | \hat{H} | \tilde{\Psi} \rangle \\ \times (1 - \langle \Psi_1 + \cdots + \Psi_{n-1} | \tilde{\Psi} \rangle / \langle \tilde{\Psi} | \tilde{\Psi} \rangle) \\ = E_{\text{MPn}} + \Delta E_{\text{PUHF}} (1 - \langle \Psi_1 + \cdots + \Psi_{n-1} | \tilde{\Psi} \rangle / \langle \tilde{\Psi} | \tilde{\Psi} \rangle) \quad (25)$$

This approximate formula works quite well when compared to equation (22) or (23), and is much simpler to compute. Because spin-unrestricted MPn energies can be substantially higher than the projected energies, the use of spin-projected MPn energies is recommended any time spin contamination is significant. Gradients for projected MPn energies have been reported¹⁴ but are not available in most quantum chemistry programs.

For QCISD, CCSD, and BD methods, the unprojected (see *Coupled-cluster Theory*) and projected^{4,12} energies can be written as

$$E = \langle \Psi_0 | \hat{H} | \Psi \rangle \quad E_{\text{proj}} = \langle \Psi_0 | \hat{P}_s \hat{H} | \Psi \rangle / \langle \Psi_0 | \hat{P}_s | \Psi \rangle \quad (26)$$

If the projector is replaced by a single annihilator, \hat{A}_k , it can be shown that the CCSD energy after single annihilation is the same as the energy without annihilation,^{12b} similar behavior is found for QCI and BD energies. Because of this, spin-unrestricted QCI, CC, and BD methods are less affected by spin contamination, and are normally used without projection.

Figure 3 shows a number of potential energy curves for hydrogen fluoride compared to full configuration interaction calculations with the same basis set.⁴ The RMP4 calculations go to the wrong limit as the bond dissociates, while UMP4 goes to the correct limit but is too high at intermediate bond lengths. PMP4, UQCI (unrestricted quadratic configuration interaction), UCC (unrestricted coupled cluster), and UBD (unrestricted Brueckner doubles) methods perform quite well for the entire range, with a maximum deviation of ~ 0.004 au from the full configuration calculations, near the onset of the RBD \rightarrow UBD instability at 2.0 Å. With the triples correction, RQCISD(T) and RCCSD(T) are somewhat better than unrestricted methods before the RBD \rightarrow UBD instability, but PMP4, UQCISD(T), UCCSD(T), and UBD(T) are better at longer bond lengths.

For spin-restricted calculations on distorted systems, such as transition states or highly strained structures, stability analysis¹⁵ can be used to determine if a UHF calculation is lower than the RHF energy. This situation is equivalent to a bond dissociation potential beyond the onset of the RHF \rightarrow UHF instability. If the lowest root of the stability matrix (lowest eigenvalue of the orbital rotation Hessian) is a small negative number, then spin-restricted correlation methods may be satisfactory. If the root is large, then the UHF determinant is significantly more stable than the RHF determinant, and spin-unrestricted methods such as PMPn, UQCI, UCC, or UBD should be used to calculate the correlation energy. For an SCF calculation to coverage to a UHF solution ($S^2 \neq 0$) rather than the RHF solution ($S^2 = 0$), the initial guess for the α and β orbitals must be different; this can be accomplished by mixing the highest occupied and lowest unoccupied orbitals in a manner similar to equation (3).

An approximate method for improving the energy by removing the contamination from a single state has been given by Yamaguchi et al.¹⁶ The energy, wavefunction, and S^2 of the spin-contaminated calculation are written in terms of the desired spin state and one higher spin state. An explicit calculation of the higher spin state, Ψ_{s+1} , is used to estimate the contribution to the energy and (\hat{S}^2) of the spin-contaminated calculation. Subtraction of the energy contribution of the higher spin state, E_{s+1} , from the spin-contaminated energy and renormalization yields an estimate of the energy of the desired pure spin state, E_s :

$$\Psi = (1 - a)\Psi_s + a\Psi_{s+1} \\ E = (1 - a)E_s + aE_{s+1} \\ \langle S^2 \rangle = (1 - a)s(s + 1) + a(s + 1)(s + 2) \quad (27) \\ a = ((S^2) - s(s + 1)) / 2(s + 1) \quad E_s = (E - aE_{s+1}) / (1 - a)$$

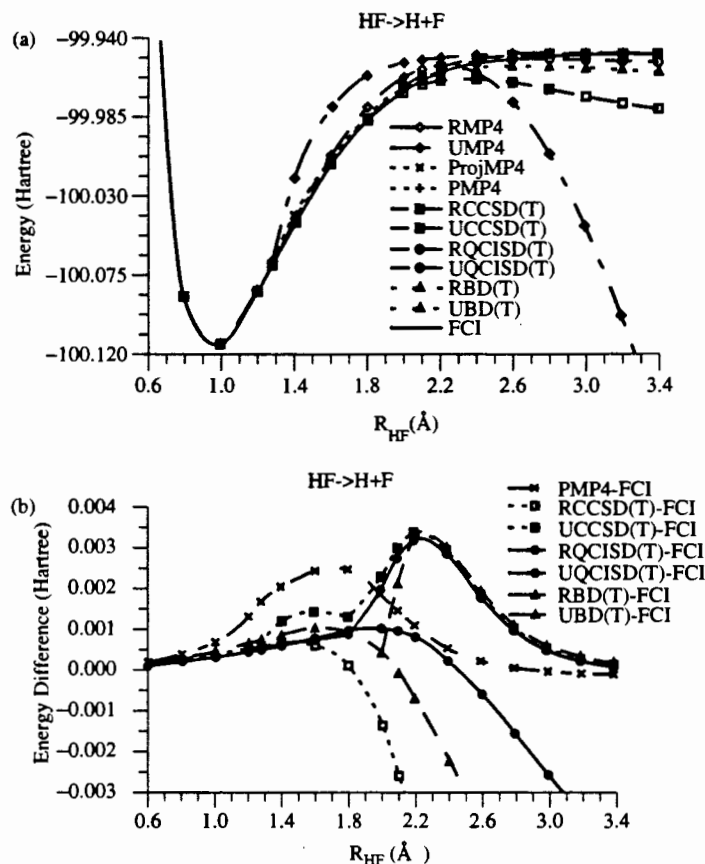


Figure 3 Bond dissociation potential for hydrogen fluoride computed at various levels of theory with the 6-31G basis set (a) total energies and (b) energy differences relative to full configuration interaction (reproduced with permission from Ref. 4)

An advantage of this approach is that it can be applied to any level of theory for which $\langle \hat{S}^2 \rangle$ can be calculated. Disadvantages include the fact that contamination is assumed to come from only one state (leading to an underestimate of the correction) and that an extra calculation is needed to determine the energy of the higher spin state.

For DFT methods, spin projection of the energy encounters the same difficulties as the calculation of S^2 . Almlöf et al.¹⁷ have suggested that the Kohn-Sham orbitals can be used to construct excited determinants and that the projected energy can be estimated using the PUHF formula, equation (20). Alternatively, the approximation of Yamaguchi et al.¹⁶ (equation 27) can be used. Figure 4 shows that the shape of an unrestricted DFT dissociation curve compares well with the full configuration interaction curve, but restricted DFT goes to the wrong limit. Similar to the PUHF calculations shown in Figure 1, the spin-projected DFT curves have a kink at the onset of the restricted \rightarrow unrestricted instability, and are not suitable for calculation of potential energy surfaces.⁹ DFT methods for radicals are much less susceptible to spin contamination problems than UHF methods, and should normally be used without projection.

The spin projection methods discussed so far apply the projection after the wavefunction has been determined. A second approach is to construct the wavefunction so that there is no spin contamination from the beginning. This leads to methods such as ROHF and restricted open-shell Møller-Plesset perturbation theory (ROMPn),¹⁸ and to valence bond, MCSCF, and CI and MRDCI methods that use spin-adapted configurations.

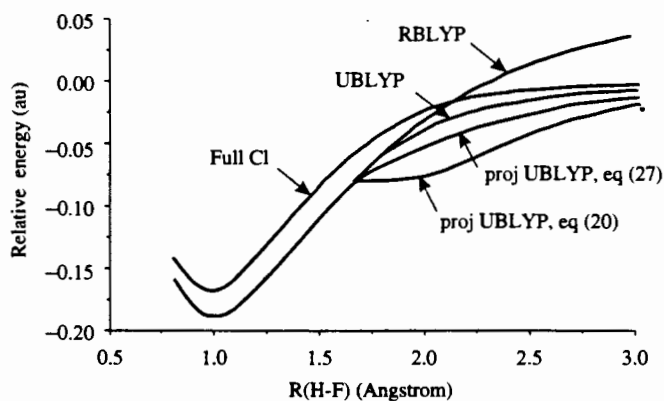


Figure 4 Bond dissociation potential for hydrogen fluoride by restricted, unrestricted, and projected density functional theory, computed with the BLYP functional and the 6-31G basis set (reproduced with permission from Ref. 9)

In addition, there are two methods that involve spin projection operators. The spin extended Hartree-Fock² (EHF) method starts with a single determinant of unrestricted spin orbitals and applies a spin projection operator before the molecular orbital coefficients are calculated in an SCF procedure. The half projected Hartree-Fock (HPHF)¹⁹ method uses a two determinantal wavefunction composed of spin-unrestricted orbitals to represent singlet and $s_z = 0$ triplet states for systems with an equal number of α and β electrons. The second determinant is

obtained from the first by exchanging the spatial parts of the α and β orbitals, and an SCF procedure is used to obtain the orbital coefficients.

A third alternative is to use projection methods during the determination of the wavefunction. Annihilated unrestricted Hartree-Fock (AUHF)²⁰ uses a projector or annihilator to remove spin contamination from the density used to construct the unrestricted α and β Fock matrices. The spin constrained Hartree-Fock method (SUHF)²¹ adds $\lambda \sum_i^{N_\alpha} |\phi_i\rangle\langle\phi_i| - |\bar{\phi}_i\rangle\langle\bar{\phi}_i|$ to the α Fock operator and $\lambda \sum_i^{N_\beta} |\bar{\phi}_i\rangle\langle\bar{\phi}_i| - |\phi_i\rangle\langle\phi_i|$ to the β Fock operator. Both methods yield orbitals with much less spin contamination than the UHF method; for $\lambda \rightarrow \infty$, the SUHF wavefunction and energy becomes the same as ROHF. The AUHF and SUHF orbitals and Fock matrices can be used in the UMP n formulas to yield the AUMP n ²⁰ and SUMP n ²¹ energies. For radicals and higher spin states, the results are comparable to the restricted open-shell calculations. However, AUHF and AUMP n methods are not suitable for open-shell singlets, such as those encountered in bond dissociations, since these methods reduce to RHF and RMP n in this situation.

In summary, spin contamination can cause problems for potential energy surfaces computed by methods based on UHF determinants. Spin projection can improve the behavior of UMP n calculations, but normally should not be used for UHF and DFT calculations. Methods such as QCISD, CCSD, and BD are much less susceptible to the effects of spin contamination.

6 RELATED ARTICLES

Configuration Interaction; Coupled-cluster Theory; Density Functional Theory (DFT), Hartree-Fock (HF), and the Self-consistent Field; Møller-Plesset Perturbation Theory.

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Spin Density

The excess electron density related to the electron with α spin over that of the electron with β spin (see *Spin-Orbital*) at a given point of an open-shell system. For a closed-shell system spin density is zero everywhere.

Spin-Orbit Coupling

The interaction of the electron spin magnetic moment with the magnetic moment due to the orbital motion of the electron, and the consequent mixing of electronic states of different multiplicity. See *Spin-coupled Theory*.

Spin-Orbital

The complete one-electron wavefunction given (in the absence or in the case of neglect of spin-orbit coupling) by a product of a spatial function (orbital) and a spin function. An orbital $\psi_i(\mathbf{r})$ may be associated with either $\alpha(\xi)$ or $\beta(\xi)$ spin functions, the spin coordinate ξ taking one of two possible values (1/2 or -1/2) measuring the spin angular momentum component along the z-axis in units of $\hbar/2\pi$. This gives rise to the spin-orbitals $\psi_i(\mathbf{r})\alpha(\xi)$ and $\psi_i(\mathbf{r})\beta(\xi)$.

Spin Polarization

A distinction is made between static and dynamic spin polarization effects. Static polarization of an electron spin occurs