

# An Orbital-Based Definition of Radical and Multiradical Character

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Received: May 11, 2004; In Final Form: August 6, 2004

A definition for radical and general  $m$ -fold multiradical character of molecular systems is formulated. The orbitals in which lone or odd electrons most often reside are identified; these orbitals are found by maximizing their probability of ( $m$ -fold simultaneous) single occupancy over orbital rotations. The maximum such probability functions as a scalar measure of (multi)radical character. The method is general and applicable to wavefunctions of any form. The radical character, as defined here, obeys strict bounds of zero and unity and has a well-defined meaning. The method has been implemented generally, and it has been tested on simple radical, diradical (biradical), and triradical systems. The results agree with chemical experience for these cases, and in the diradical case, we show that it agrees qualitatively with earlier proposed characterization schemes. Specific implementation for monoradical character requires only two-particle density matrix information, and furthermore, a promising approximation for the diradical analogue can be constructed from quantities that we call the first and second monoradical characters and orbitals. An algebraic connection can be made to a reinterpretation of the widely discussed distribution of total odd electrons.

## 1. Introduction

Radical behavior is a phenomenon familiar to every chemist, and it is of great general interest, because much of chemistry proceeds through pathways involving radicals. However, radical character, like aromaticity and bond order, belongs to a class of intuitive chemical concepts which do not have unique theoretical definitions.

The electron pair was first proposed in a 1916 article by Lewis.<sup>1</sup> In this early work, the role of unpaired or odd electrons was discussed in order to explain valency and reactivity. Quantum mechanics and resulting orbital theories have much elucidated the physical nature of electron pairing,<sup>2</sup> but the discussion of fundamental properties of pairing and their impact on chemistry is still proceeding in the modern literature.<sup>3–7</sup>

There is no quantum mechanical operator which defines the extent of pairing unambiguously. Consequently, there can be no direct measurement of radical character. One can only observe behaviors of molecules believed to be characteristic of radicals and infer information about their electronic structure. Experimental characterization of radicals is often based on measurements of spin properties of their unpaired electrons.<sup>5</sup> The total spin angular momentum per molecule can be determined by measuring bulk magnetization as a function of applied static magnetic field at very low temperature. Electron spin resonance is a critical spectroscopic tool to determine the ground-state spin multiplicity, in which the interaction of unpaired electrons with external (usually microwave) radiation gives rise to characteristic signals. Spin-state energy gaps are also used to characterize radicals. In particular, the singlet–triplet splitting is one of the most widely used indicators of diradical character,<sup>8</sup> and this will be discussed from a theoretical point of view later. Site-specific reactivity is also a primary

characteristic of radicals; reactivity can be studied by measuring species lifetimes using transient absorption spectroscopy.<sup>9</sup>

It has been the challenge of theory to develop a quantitative measure of radical character which agrees with the qualitative understanding of electron pairing in chemical and quantum mechanical contexts.

In molecular orbital theory, a radical is understood simply by the presence of a singly occupied orbital. Beyond the Hartree–Fock approach, however, one of the most basic and widely understood ways to quantitatively think about radical character is to look at natural orbital occupations directly. Radicals are indicated by occupations that differ significantly from zero or two, which are the only values present for closed-shell, single-determinant wavefunctions. For example, occupation of a LUMO-like orbital by nearly one electron on the average is characteristic of a singlet diradical; because of the close connection between natural orbitals and bonding/antibonding orbitals, this occupation is usually a manifestation of a mostly broken bond, which leads to spin-entangled radical fragments at dissociation. This is discussed thoroughly by Döhnert and Koutecký.<sup>10</sup>

In a 1978 paper by Takatsuka, Fueno, and Yamaguchi,<sup>11</sup> the distribution operator

$$\hat{D} = 2(\hat{\rho}) - (\hat{\rho})^2 \quad (1)$$

was proposed for singlet systems, where  $\hat{\rho}$  is the spinless one-particle density operator. Similar formulas were proposed for higher-spin systems. The formula was proposed on the somewhat heuristic argument that every matrix element of this operator is identically zero for a state that can be represented as a single, closed-shell determinant. Otherwise,  $\hat{D}$  identifies the regions of space where the wavefunction is not closed-shell-like. The diagonal elements of this operator,  $D(\vec{r}) = \langle \vec{r} | \hat{D} | \vec{r} \rangle$ ,

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are said to be a spatial distribution of total odd electrons. The integral over  $D(\vec{r})$  has been used<sup>11,12</sup> to define the total number of unpaired electrons,  $n_D = \text{Tr}(\hat{D})$ .

An elegantly presented motivation for  $\hat{D}$  was constructed twenty years later, but apparently independently, by Bochicchio.<sup>13</sup>  $D(\vec{r})$  is interpreted there as a hole distribution, deriving its name from the construction of a hole density operator ( $2 - \hat{\rho}$ ) contracted with the particle density operator, obtaining an expectation value for the number of holes in a conventional trace algebra formulation. The result is that  $\hat{D}$  is a second-order operator in  $\hat{\rho}$ . In contracting the hole density with the particle density, however, a hole is only counted if there is some nonzero particle density in that same natural orbital. For small occupations, the orbital is counted as a nearly double hole (weighted by the small occupancy).

Although eq 1 has largely the correct behavior when the eigenvalues of  $\hat{\rho}$  are all zero, one, or two, its behavior at other points is somewhat arbitrary, as pointed out by Head-Gordon.<sup>14</sup> The limit, shown by Staroverov and Davidson,<sup>12</sup> in which one might determine that a molecule has  $n_D = 2n$  unpaired electrons, or  $2n$  electron holes, is particularly unphysical ( $n$  is the number of electrons). An attempt to correct this by modifying  $\hat{D}$  has been made.<sup>14</sup> In light of this strange limiting behavior, it is difficult to say rigorously what the exact interpretation of  $\hat{D}$  or  $D(\vec{r})$  should be.

Recent work has also made use of the electron localization function (ELF)<sup>15</sup> applied to spin densities and total densities,<sup>16</sup> and the resulting plots show interesting density anomalies in the regions where one would expect to find odd electrons, at dangling bonds. However, it is not clear that this analysis rigorously corresponds to the presence of lone electrons.

We would like to draw attention to work on radicals by some of the present authors and others. These studies involve either accurate computation or analysis of multiradicals, and they make use of the principle which we will attempt to define generally in this work. That principle is that radical character is best analyzed with respect to specific radical orbitals, which are singly occupied, or, more generally, have a high probability of being singly occupied.

In work by Jung and Head-Gordon,<sup>17,18</sup> a perfect-pairing cluster amplitude can be used to obtain the weight of an important (diradical) correlating transition easily. This transition implicitly defines radical orbitals as mixtures of the HOMO and LUMO, as discussed later. Slipchenko and Krylov<sup>19</sup> obtain triradical orbitals by looking at the high-spin analogue of a system of interest at the Hartree–Fock level and then flipping the spin of one electron in a correlation calculation for the low-spin case (spin-flip coupled cluster). We should also acknowledge the well-known work of Amos and Hall,<sup>20</sup> who define corresponding orbitals in unrestricted Hartree–Fock wavefunctions with broken symmetry; this is conceptually similar to our own work but not as general.

There is a natural inclination to use electron spin as a theoretical tool to characterize radicals. Although there is a clear connection between singly occupied orbitals and the presence of a nonzero spin density, we argue that models of radical character based on spin alone are insufficient to generalize the concept of radicals, diradicals, and so on, to complicated wavefunctions. For example, the common notion of a singlet diradical<sup>3–7</sup> involves a molecule whose spin density is zero everywhere. In any system with more than two electrons, it is impossible to consider any two as spin paired, because all coordinates of the indistinguishable electrons play equivalent

roles in the wavefunction. Indeed, the two-particle spin density matrix generally has  $\downarrow\downarrow$ ,  $\uparrow\uparrow$ , and  $\uparrow\downarrow + \downarrow\uparrow$  blocks, as well as the singlet paired  $\uparrow\downarrow - \downarrow\uparrow$  block. For these reasons, it is necessary to look beyond just spin to describe the chemical phenomenon known as pairing, although the singlet–triplet energy gap will be of considerable interest in characterizing diradicals within our proposed model. Electrons in doubly occupied orbitals cannot rigorously be said to form a spin singlet, however; we would like to preserve the concept that a doubly occupied orbital pairs electrons.

We propose an orbital-based definition of radical character on the grounds of the following physical argument. The phenomenologically conjectured electron pair is a consequence of the Pauli exclusion principle, because electrons cannot form groups of greater than two in lower-energy spatial orbitals. If two molecules, fragments, or atoms are each individually described by singly occupied orbitals, then the ground-state wavefunction of the combined system should involve a bonding interaction between them. The bond results from the fact that there are only enough electrons to fill the bonding combination formed from the originally singly occupied orbitals. The ability to find an orbital in a molecule that has a high probability of being singly occupied indicates that a large portion of the wavefunction should be conducive to such a bonding interaction. We should then have an indicator of the reactivity of a molecule, which is a primary characteristic of a radical, in the spirit of Lewis's original concept of pairing.

## 2. Definition

The radical character of a spatial orbital  $|\phi_s\rangle$  is defined as the probability of single occupancy of that orbital,  $P_1$ , which can formally be written as the expectation value of a Hermitian operator

$$P_1(|\phi_s\rangle) = \langle \Psi | (\hat{n}_{s\downarrow}^\circ \hat{n}_{s\downarrow}^\bullet + \hat{n}_{s\uparrow}^\circ \hat{n}_{s\uparrow}^\bullet) | \Psi \rangle \quad (2)$$

where  $\hat{n}^\bullet$  and  $\hat{n}^\circ$  are the particle- and hole-number operators, respectively, acting on spin orbitals  $|\phi_s, \downarrow\rangle$  and  $|\phi_s, \uparrow\rangle$ , and  $|\Psi\rangle$  is the many-electron, multideterminant state of interest. The product of number operators measures the probability that  $|\phi_s\rangle$  is occupied by a  $\downarrow$  electron but not a  $\uparrow$  electron, or vice versa. We take the monoradical character of a molecule,  $R_1 = P_1^{\text{opt}}$ , to be the radical character of the most radical orbital in that molecule  $|\phi_s\rangle^{\text{opt}}$ . In practice, this is found by optimizing  $P_1$  over continuous rotations of  $|\phi_s\rangle$  with all other spatial orbitals spanning the one-particle space.

Our formalism for computing single occupancy is independent of needing an excess spin density to extract such information. It can be shown that the form of the operator in eq 2 is invariant with respect to any real or complex rotation of the spin basis in which it is written, making the probability of single occupancy of an orbital a well-defined physical quantity for a given wavefunction, independent of the direction chosen to be up.

All of the information necessary to compute the monoradical character and orbital, including derivatives of  $P_1$  with respect to orbital rotation, is obtainable from the two-particle density operator,  ${}^2\hat{\rho}$ .  ${}^2\hat{\rho}$  is necessary, because evaluating single occupancy involves the simultaneous knowledge of both a particle and a hole. One can use the definitions of the particle and hole operators in terms of the normal annihilation and creation operators,  $\hat{a}$  and  $\hat{a}^\dagger$ , respectively

$$n_{s\downarrow}^\bullet = \hat{a}_{s\downarrow}^\dagger \hat{a}_{s\downarrow}, \quad n_{s\downarrow}^\circ = \hat{a}_{s\downarrow} \hat{a}_{s\downarrow}^\dagger \quad (3)$$

and the anticommutation

$$\hat{a}_{s\downarrow}\hat{a}_{s\downarrow}^\dagger = 1 - \hat{a}_{s\downarrow}^\dagger\hat{a}_{s\downarrow} \quad (4)$$

to obtain

$$\begin{aligned} P_1(|\phi_s\rangle) &= \langle\Psi|(\hat{a}_{s\downarrow}^\dagger\hat{a}_{s\downarrow} + \hat{a}_{s\uparrow}^\dagger\hat{a}_{s\uparrow} - 2\hat{a}_{s\downarrow}^\dagger\hat{a}_{s\downarrow}\hat{a}_{s\uparrow}^\dagger\hat{a}_{s\uparrow})|\Psi\rangle \\ &= \langle\Psi|(\hat{n}_{s\downarrow}^* + \hat{n}_{s\uparrow}^* - 2\hat{n}_{s\downarrow}^*\hat{n}_{s\uparrow}^*)|\Psi\rangle \end{aligned} \quad (5)$$

An interpretation follows from the second line of eq 5. The probability of single occupancy of  $|\phi_s\rangle$  is the probability of occupancy of  $|\phi_{s\downarrow}\rangle$  plus the occupancy of  $|\phi_{s\uparrow}\rangle$ , minus the probability that we counted the  $\downarrow$  orbital while the  $\uparrow$  orbital was occupied, which is the same as the probability that we counted the  $\uparrow$  orbital while the  $\downarrow$  orbital was occupied, hence the factor of 2 for the two-particle piece. Because computing  $R_1$  depends only on the information in  ${}^2\rho$ , computing this quantity should be feasible for any system for which the energy can be computed. Derivatives of  $P_1$  are presented in the method section. Interestingly, Takatsuka et al. acknowledge that “recourse to the second-order density matrix would be unavoidable” when  $D(\bar{r})$  fails to give a good characterization.

One of the advantages of this definition is that it generalizes easily to the diradical case

$$P_2(\{|\phi_1\rangle, |\phi_2\rangle\}) = \langle\Psi|(\hat{n}_{1\downarrow}^*\hat{n}_{1\uparrow}^* + \hat{n}_{1\uparrow}^*\hat{n}_{1\downarrow}^*)(\hat{n}_{2\downarrow}^*\hat{n}_{2\uparrow}^* + \hat{n}_{2\uparrow}^*\hat{n}_{2\downarrow}^*)|\Psi\rangle \quad (6)$$

which is the probability of simultaneous single occupancy of two orthonormal spatial functions  $|\phi_1\rangle$  and  $|\phi_2\rangle$ , where we have chosen the indices 1 and 2 for convenience. Under this definition, infinitely stretched singlet  $H_2$  is perfectly diradical, and the orbitals which maximize  $P_2 \rightarrow R_2$  are the atomic  $|1s_A\rangle$  and  $|1s_B\rangle$  functions on protons A and B, respectively.  $|1s_A\rangle$  and  $|1s_B\rangle$  are both singly occupied in every configuration when the wavefunction is written in that basis. The states  $|1\sigma\rangle$  and  $|1\sigma^*\rangle$

$$\frac{|1s_A\downarrow 1s_B\uparrow\rangle + |1s_B\downarrow 1s_A\uparrow\rangle}{\sqrt{2}} = \frac{|1\sigma\downarrow 1\sigma\uparrow\rangle - |1\sigma^*\downarrow 1\sigma^*\uparrow\rangle}{\sqrt{2}} \quad (7)$$

are the bonding and antibonding orbitals, respectively. We insist on an orthonormal pair of orbitals for the optimization in the diradical case, or else, we would simply obtain two copies of the most radical orbital from the monoradical evaluation.

The generalization of the definition to the  $m$ -fold multiradical case is ( $m = 1$  for monoradical,  $m = 2$  for diradical, etc.)

$$\begin{aligned} P_m(\{|\phi_1\rangle, |\phi_2\rangle, \dots, |\phi_m\rangle\}) &= \langle\hat{P}_m(\{|\phi_1\rangle, |\phi_2\rangle, \dots, |\phi_m\rangle\})\rangle = \\ &= \langle\Psi|\left[\prod_{s=1}^m(\hat{n}_{s\downarrow}^*\hat{n}_{s\uparrow}^* + \hat{n}_{s\uparrow}^*\hat{n}_{s\downarrow}^*)\right]|\Psi\rangle \end{aligned} \quad (8)$$

for a set of  $m$  orthonormal spatial orbitals, where we are concerned with the probability of simultaneous single occupancy of those orbitals. Again, these orbitals are optimized to obtain the  $m$ -fold multiradical character  $R_m = P_m^{\text{opt}}$  of the molecule in question, which is the probability of finding the optimal orbitals 1 through  $m$  simultaneously singly occupied.

Because of the cost of generalizing this method to higher multiradical character, it is most applicable only to monoradicals and diradicals. We can show that fully evaluating the  $m$ -fold multiradical character needs the  $2m$ -particle density matrix, which is usually an expensive quantity to obtain or manipulate.

There is hope, however, to get a good approximation of the diradical character from monoradical information, without the four-particle density matrix. If we know that the monoradical orbital  $|\phi_1\rangle^{\text{opt}}$  in an even electron system has probability  $R_1$  of being singly occupied, then we know that there is at least one other electron alone in an orbital somewhere else, in all configurations where only one electron is in  $|\phi_1\rangle^{\text{opt}}$ . However, we would like to know that the other electron is alone in the same orbital  $|\phi_2\rangle^{\text{opt}}$  in each one of those configurations, as a condition for the monoradical and diradical characters to be related. We will look at this hypothesis with respect to the quantities we call the first and second monoradical orbitals and characters. The first monoradical orbital and character are exactly  $|\phi_1\rangle^{\text{opt}}$  and  $R_1$ , respectively, as defined and discussed to this point. The second monoradical character  $R_1^{(2)} = P_1^{(2)\text{opt}}$  is defined as the probability that the second monoradical orbital  $|\phi_2\rangle^{\text{opt}}$  is singly occupied, such that  $P_1^{(2)}$  has been optimized subject to the constraint that the orbitals are orthonormal,  $\langle\phi_2|\phi_1\rangle^{\text{opt}} = 0$ .

### 3. Method

To avoid construction of a general  $2m$ -particle density matrix algorithm, it is easiest to write code in the spirit of the first quantization, when  $m$  is an input parameter. That is to say that the state  $|\Psi\rangle$  is expressed as a list of coefficients of each of the possible determinants of orbitals in a given orthonormal single-particle basis. As the single-particle basis is rotated, the same many-particle function space is spanned by the determinants of the new orbitals, and the state is re-expressed as a list of coefficients for the new determinants.

It is trivial to decide whether an orbital  $|\phi_q^i\rangle$  of the  $i^{\text{th}}$  rotated basis  $\{|\phi_q^i\rangle | 1 \leq q \leq N\}$  is empty, singly occupied, or doubly occupied in each possible determinant of these orbitals ( $N$  is the number of spatial basis functions). For the  $m$ -fold multiradical character, we are concerned with the probability of simultaneous single occupancy of a set of  $m$  orbitals. For convenience, we establish the convention that these orbitals are the first  $m$  members of the complete set,  $\{|\phi_s^i\rangle | 1 \leq s \leq m\} \subset \{|\phi_q^i\rangle\}$ . These first  $m$  orbitals will be called the trial orbitals, and the remaining orbitals are referred to as the complementary trial, or c-trial, orbitals. The index  $s$  henceforth refers to a member of the trial orbitals, and the indices  $p$  and  $q$  refer to either a trial or c-trial orbital. The trial orbitals yielding the maximum of  $P_m$  are the radical orbitals  $\{|\phi_s^i\rangle^{\text{opt}}\}$ , and the maximum possible value of  $P_m$  defines  $R_m$ .

If a certain determinant in the ket  $|\Psi\rangle$  has all members of  $\{|\phi_s^i\rangle\}$  singly occupied, then that determinant contributes to the radical character of those trial orbitals. In other words, the determinant survives being operated on by  $\hat{P}_m(\{|\phi_s^i\rangle\})$  of eq 8, and it projects onto itself in the bra  $\langle\Psi|$ . The function value  $P_m(\{|\phi_s^i\rangle\})$  is then computed as the sum of squares of the coefficients of those determinants, wherein the subset of  $m$  orbitals are all singly occupied, as in eq 9. Essentially, we get the norm-squared of a projection of  $|\Psi\rangle$  (a probability) into a subspace of radical determinants,  $\text{span}\{|\Phi_x^{m-\text{Rad}}(\{|\phi_q^i\rangle\})\}$ . Note, however, that this subspace is variable, depending on the rotation of the orbitals.

$$\begin{aligned} P_m(\{|\phi_s^i\rangle\}) &= \langle\Psi|\left[\sum_x|\Phi_x^{m-\text{Rad}}(\{|\phi_q^i\rangle\})\right]\langle\Phi_x^{m-\text{Rad}}(\{|\phi_q^i\rangle\})|\Psi\rangle \\ &= \sum_x \langle\Psi|\Phi_x^{m-\text{Rad}}(\{|\phi_q^i\rangle\})\rangle^2 \end{aligned} \quad (9)$$

We define rotation coordinates  $(\theta_i)_{p'}^i$  between orbitals  $|\phi_p^i\rangle$  and  $|\phi_{p'}^i\rangle$  at each  $i^{\text{th}}$  iteration. To first order in  $(\theta_i)_{p'}^i$ , the  $p^{\text{th}}$  orbital takes on a component in the direction of the  $p^{\text{th}}$  orbital and the  $p'^{\text{th}}$  orbital takes on a negative component in the  $p^{\text{th}}$  orbital. As a matter of notation, we define the upper index  $p'$  to be the greater one,  $p' > p$ . The vector  $\theta_i$  holds all the local  $[N(N-1)/2]$  instantaneous pairwise rotation coordinates. We then construct the gradient vector with respect to these coordinates. We note that at least one of the indices of a gradient component must denote a trial orbital to obtain a nonzero result for that component. There are nonzero derivatives for both trial/trial and trial/c-trial mixings.

$$\frac{\partial P_m}{\partial(\theta_i)_s^p} \Big|_{\theta_i=0} = \sum_x 2 \langle \Psi | \Phi_x^{m-\text{Rad}}(\{|\phi_q^{i-1}\rangle\}) \rangle \times \langle \Psi | \left[ \frac{\partial}{\partial(\theta_i)_s^p} | \Phi_x^{m-\text{Rad}}(\{|\phi_q^i\rangle\}) \right] \Big|_{\theta_i=0} \quad (10)$$

In each determinant  $|\Phi_x^{m-\text{Rad}}(\{|\phi_q^i\rangle\})\rangle$ , the trial orbital  $|\phi_s^i\rangle$  is singly occupied by either a  $\downarrow$  or  $\uparrow$  electron in order that it is a member of the set of radical determinants, but  $|\phi_{p'}^i\rangle$  is empty, doubly occupied, or singly occupied, in general. Choosing arbitrarily for  $|\phi_s^i\rangle$  to be singly occupied by a  $\downarrow$  electron, we have four possibilities for the occupancy of  $|\phi_{p'}^i\rangle$  and, consequently, four possibilities for the derivative of each radical determinant with respect to any  $(\theta_i)_s^p$ .

$$\begin{aligned} \text{(a)} \quad & \frac{\partial}{\partial(\theta_i)_s^p} | \dots \phi_s^i \downarrow \dots \rangle \Big|_{\theta_i=0} = | \dots \phi_p^{i-1} \downarrow \dots \rangle \\ \text{(b)} \quad & \frac{\partial}{\partial(\theta_i)_s^p} | \dots \phi_s^i \downarrow \dots \phi_{p'}^i \downarrow \dots \rangle \Big|_{\theta_i=0} = 0 \\ \text{(c)} \quad & \frac{\partial}{\partial(\theta_i)_s^p} | \dots \phi_s^i \downarrow \dots \phi_{p'}^i \uparrow \dots \rangle \Big|_{\theta_i=0} = | \dots \phi_p^{i-1} \downarrow \dots \phi_{p'}^{i-1} \uparrow \dots \rangle - \\ & | \dots \phi_s^{i-1} \downarrow \dots \phi_{p'}^{i-1} \uparrow \dots \rangle \\ \text{(d)} \quad & \frac{\partial}{\partial(\theta_i)_s^p} | \dots \phi_s^i \downarrow \dots \phi_{p'}^i \downarrow \phi_{p'}^i \uparrow \dots \rangle \Big|_{\theta_i=0} = | \dots \phi_p^{i-1} \downarrow \dots \phi_s^{i-1} \downarrow \phi_s^{i-1} \uparrow \dots \rangle \end{aligned} \quad (11)$$

In eq 11b, the determinants composing the derivative are zero by antisymmetry. In eq 11d, permutational antisymmetry is used to arrive at the final expression.

The derivative algorithm functions similarly to the algorithm for the evaluation of  $P_m$ . For each radical determinant  $|\Phi_x^{m-\text{Rad}}(\{|\phi_q^{i-1}\rangle\})\rangle$ , the coefficient of this determinant is multiplied by the coefficients of the determinants into which it rotates with each  $(\theta_i)_s^p$ , per eq 10. Each product then contributes to the corresponding component of the gradient. A conjugate-gradient-like algorithm is used to optimize  $P_m$ . Parallel transport of the previous step information, resulting from the change of rotational coordinates at each step, is neglected in this algorithm; this is acceptable for the small steps near convergence; the initial large steps were done by steepest descent.

We can also express the components of the gradient of the monoradical character on the space of  $\theta_i$  in second quantized

form. We differentiate the operators in the first line of eq 5

$$\frac{\partial}{\partial(\theta_i)_s^p} \hat{a}_{s(i)}^\dagger \Big|_{\theta_i=0} = \hat{a}_{p(i-1)^\dagger} \quad \frac{\partial}{\partial(\theta_i)_s^p} \hat{a}_{s(i)}^\dagger \Big|_{\theta_i=0} = \hat{a}_{p(i-1)^\dagger} \quad (12)$$

to obtain

$$\begin{aligned} \frac{\partial P_1}{\partial(\theta_i)_s^p} \Big|_{\theta_i=0} &= \langle \Psi | (\hat{a}_{p'}^\dagger \hat{a}_{s^\dagger} + \hat{a}_{s^\dagger}^\dagger \hat{a}_{p'} + \hat{a}_{p'}^\dagger \hat{a}_{s^\dagger} + \hat{a}_{s^\dagger}^\dagger \hat{a}_{p'} - \\ & 2\hat{a}_{p'}^\dagger \hat{a}_{s^\dagger} \hat{a}_{s^\dagger}^\dagger \hat{a}_{s^\dagger} - 2\hat{a}_{s^\dagger}^\dagger \hat{a}_{p'} \hat{a}_{s^\dagger}^\dagger \hat{a}_{s^\dagger} - 2\hat{a}_{s^\dagger}^\dagger \hat{a}_{s^\dagger} \hat{a}_{p'}^\dagger \hat{a}_{s^\dagger} - 2\hat{a}_{s^\dagger}^\dagger \hat{a}_{s^\dagger} \hat{a}_{s^\dagger}^\dagger \hat{a}_{p'} \rangle | \Psi \rangle \end{aligned} \quad (13)$$

This is clearly a function of  $1\hat{\rho}$  and  $2\hat{\rho}$  only, as claimed previously. The indices  $s$  and  $p$  on the right-hand side of eq 13 refer implicitly to orbitals of the  $(i-1)^{\text{th}}$  set, as the derivative is evaluated at  $\theta_i = 0$ . Equation 13 can be shown to be equivalent to the result of eq 11 when inserted into eq 10.

This optimization algorithm has been implemented as an extension to a development version of the *Q-Chem* program package.<sup>21</sup>

## 4. Results and Discussion

The implications of the present definition of radical and multiradical character will be discussed in a series of simple examples. Orbital optimization and a principle nuance of the radical character value will be illustrated in the context of monoradical character. The most detailed discussion of this model will take place in the consideration of diradicals. A simple triradical system demonstrates the generality of the model. The ability to approximate diradical (or higher) character from monoradical characters is motivated by a numerical example. Finally, we will highlight an interesting mathematical connection between our definition and  $\hat{D}$  for perfect-pairing wavefunctions.

**4.1. Monoradical Character.** We will consider the monoradical character of the Li atom in a 6-31G basis set (one  $s$  shell, two  $sp$  shells). A full configuration interaction (FCI) computation was done for the ground state in the doublet,  $M_S = -1/2$  space. In this example, FCI is a formality, because the state is dominated by the Hartree-Fock  $1s^2 2s^1$  configuration ( $|\text{coeff}| = 0.99995$ ). In Figure 1, the surface of the sphere represents all possible normalized single-particle functions which lie in the space spanned by the  $|1s\rangle$ ,  $|2s\rangle$  and  $|3s\rangle$  canonical orbitals. Orbital radical character  $P_1$  as a function of mixtures of these three orbitals is plotted on the sphere. As expected, the  $|1s\rangle$  and  $|3s\rangle$  orbitals have nearly zero probability of being singly occupied, because they are almost always doubly occupied or empty, respectively. The intuitive result is returned, in that the orbital that maximizes the monoradical character of the atom is approximately the  $|2s\rangle$  orbital, having nearly unit probability of being singly occupied,  $R_1 = P_1^{\text{opt}} \approx 1$ . We say that  $|2s\rangle$  is the radical orbital for Li. The function is relatively well-behaved in this simple system, making orbital optimization from an arbitrary guess a smooth process.

An important nuance of our definition is illustrated by the value of  $P_1$  along the geodesic path between the  $|1s\rangle$  and  $|3s\rangle$  orbitals. The peak radical character along this path is

$$P_1 \left( \frac{(|1s\rangle + |3s\rangle)}{\sqrt{2}} \right) \approx 0.5 \quad (14)$$



**Figure 1.** Radical character as a function of orbital for the FCI/6-31G Li atom [0  $\approx$  black < gray < purple < dark blue < light blue < green < yellow < orange  $\approx$  1]. The  $|1s\rangle$  and  $|3s\rangle$  orbitals have nearly zero probability of being singly occupied, as is true for the  $|2p\rangle$  and  $|3p\rangle$  functions that cannot be shown here. The  $|2s\rangle$  orbital has almost unit probability of being singly occupied, and one expects it to be the radical orbital for Li. Orbitals which are mixtures of these bases have intermediate values for the probability of single occupancy.

To illustrate the meaning of this, consider the basis

$$|\phi_1\rangle = \frac{|1s\rangle + |3s\rangle}{\sqrt{2}}, \quad |\phi_2\rangle = |2s\rangle, \quad |\phi_3\rangle = \frac{|1s\rangle - |3s\rangle}{\sqrt{2}} \quad (15)$$

Because  $|1s\rangle = (|\phi_1\rangle + |\phi_3\rangle)/\sqrt{2}$ , the state transforms mostly as

$$|1s\downarrow 1s\uparrow 2s\downarrow\rangle = \frac{|\phi_1\downarrow\phi_1\uparrow\phi_2\downarrow\rangle + |\phi_1\downarrow\phi_3\uparrow\phi_2\downarrow\rangle + |\phi_3\downarrow\phi_1\uparrow\phi_2\downarrow\rangle + |\phi_3\downarrow\phi_3\uparrow\phi_2\downarrow\rangle}{2} \quad (16)$$

and we can see directly that homogeneous mixtures of  $|1s\rangle$  and  $|3s\rangle$  (i.e.,  $|\phi_1\rangle$  and  $|\phi_3\rangle$ ) both have a half probability of being singly occupied. We then notice that whenever one electron is in  $|\phi_1\rangle$  there is an equal amplitude for finding another electron in  $|\phi_1\rangle$  or in  $|\phi_3\rangle$ , and vice versa when there is an electron in  $|\phi_3\rangle$ . This is a manifestation of the lack of correlation of electrons in a single-determinant wavefunction (here, specifically, in-out correlation). We have introduced the use of the  $|3s\rangle$  state to look at a determinant which is described by the  $|1s\rangle$  and  $|2s\rangle$  states. The logical extreme of this procedure is to introduce a complete basis for the analysis. If we chose the point-like position functions, we would see the lack of correlation spread over many states, but none of these states would have significant occupancy. Presumably, if a molecule's behavior is well described in the basis used for the energetic computation, then so are the radical orbitals, assuming that they are, in fact, physical indicators of reactivity.

For any system described by a single, closed-shell determinant, one can show that the monoradical character  $R_1$  of the molecule is always exactly one-half. Consider that any orbital, including the radical orbital, can be uniquely decomposed as the sum of its projections into the occupied and virtual spaces. The occupied component (renormalized) necessarily describes a doubly occupied orbital, and the virtual component describes an empty orbital. Now, we take these two states as the bases for a two-dimensional space and note that the states in this space with the highest probability of single occupancy are the

homogeneous linear combinations of the occupied and virtual bases, and that these orbitals have exactly a one-half probability of being singly occupied. Therefore, the radical orbital (which maximizes  $P_1$ ) must be a homogeneous combination of an occupied and a virtual orbital for a closed-shell determinant, and we have  $R_1 = 0.5$ .

We note for our coming discussion of diradical character that the two orthogonal homogeneous combinations ( $\pm$ ) are also simultaneously singly occupied with a probability of one-half for a closed-shell determinant, making the  $R_2$  value at least one-half. Because it is logically bounded from above by the monoradical character, we have  $R_2 = 0.5$  exactly. The transformation of the Li atom core in eq 16 illustrates the way that a general closed-shell determinant could be transformed to get  $R_2 = R_1 = 0.5$ .

There is nothing fundamental about any particular representation of a wavefunction, but usually, chemists choose a canonical representation in which member orbitals may most often be described as doubly occupied; these orbitals have particular chemical relevance. Also interesting are these radical orbitals that can be found to have a high probability of being singly occupied. From what we have learned thus far, however, this probability must exceed one-half to be chemically relevant.

**4.2. Diradical Character: General Discussion.** The generalization of the perfect-pairing analysis of Jung and Head-Gordon<sup>17</sup> for singlet diradicals to general wavefunctions was the motivation for this work. In a perfect-pairing coupled cluster doubles (PP-CCD) wavefunction,<sup>22,23</sup> each independent pair function has the form of the right-hand side of eq 7, except that the amplitude of the double excitation into the virtual orbital is a variable,  $t$ . In the basis which homogeneously mixes the HOMO and LUMO orbitals (similar to the left-hand side of eq 7), the wavefunction looks increasingly diradical with increasing magnitude of the HOMO–LUMO amplitude, explicitly  $I_{\text{HOMO}^{\text{L}}\text{HOMO}^{\text{L}}}$ . Jung and Head-Gordon quantify this effect by the LUMO occupation number following Döhnert and Koutecký.<sup>10</sup>

To illustrate the nature of a diradical with reference to our definition, we present the following discussion of two electrons in the HOMO (H) and LUMO (L) space (2-in-2), where H and L are well separated energetically from the other orbitals. H and L are canonical orbitals, meaning that they maximize the orbital energy splitting of any two orthogonal orbitals which can be constructed in this space. The singlet space for this system is spanned by three possible configuration states, whose spatial parts are HH, LL, and  $(\text{HL} + \text{LH})/\sqrt{2}$ . There is also a degenerate spin triplet of states, which all share the same spatial wavefunction,  $(\text{HL} - \text{LH})/\sqrt{2}$ . In the singlet space, the diradical character varies continuously from zero to unity, as a function of the coefficients of the three spatial wavefunctions, as in Figure 2. The triplet states, however, are all completely diradical (in any representation mixing H and L); they share the same spatial part, and two same-spin electrons cannot be in the same one-particle state.

If the HOMO–LUMO gap is large, then the aufbau principle dominates, and the system is a closed-shell singlet, with two electrons in H ( $R_2 = 0.5$ ). As the orbital splitting decreases, as when  $\text{H}_2$  is stretched, scatterings to the other singlet states become more accessible, and they mix in. Electron correlation then becomes a large effect, and the position of an electron in one localized orbital will correlate with the other electron being in the remaining orthonormal orbital; the system will then look increasingly diradical in the basis which most localizes the orbitals in the two-dimensional, one-particle space. One could



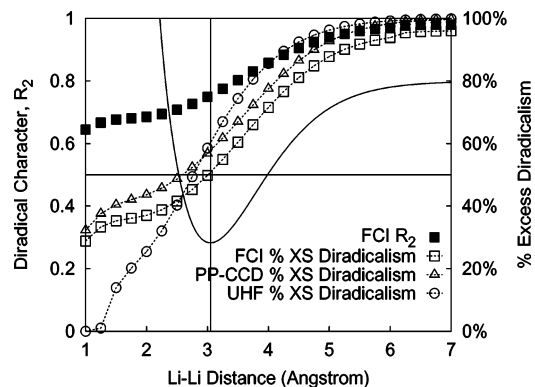
**Figure 2.** The diradical character of singlet 2-in-2 wavefunctions [The HH and LL bases have been mixed to show the cylindrical symmetry of the plot; a factor of  $1/\sqrt{2}$  is implicit.  $0 \approx \text{black} < \text{gray} < \text{purple} < \text{dark blue} < \text{light blue} < \text{green} < \text{yellow} < \text{orange} \approx 1$ ]. There exists one wavefunction in the singlet space (the north/south pole of the plot), for which no orbital in the HOMO–LUMO space is ever singly occupied; the electrons have coalesced in this wavefunction. There is a one-dimensional manifold of singlet states (the equator), for which some pair of orbitals can be found, which are always simultaneously singly occupied.

say that this effect defines the notion of localization for these purposes.

If a singlet state were completely diradical, then its spatial wavefunction would resemble that of a triplet, and therefore, the exchange contribution to the energy (Hund's rule, assuming the orbitals are near one another) would then unambiguously favor a spin-state change to a triplet state. If the HOMO–LUMO gap is significant, however, the energy favorability of allowing both electrons simultaneously into H some of the time will keep the state a singlet, but the state is then, by this same argument, not purely diradical. As a consequence of all this, no ground-state singlet should ever be completely diradical, but a singlet wavefunction can have variable diradical character, reflecting what is often called static correlation. These Hund's and aufbau contributions compete equally at the point where the singlet and triplet are degenerate. This should make the singlet–triplet energy gap a good experimental indicator of diradical character, according to our definition.

Our definition has some nice properties, relative to approaches using  ${}^1\hat{\rho}$ , that we will expound upon in the diradical case.  ${}^1\hat{\rho}$  loses interesting information about the correlation. Consider infinitely stretched  $\text{H}_2$  and the wavefunction in eq 7. Both the atomic functions and the canonical molecular orbitals diagonalize the nonzero block of the spinless one-particle density matrix in this particular case, with two degenerate eigenvalues of unity.  ${}^1\hat{\rho}$  cannot distinguish between an orbital which is singly occupied with full probability, like the atomic functions, and an orbital which is doubly occupied with a one-half probability, like the canonical functions. For any stretch distance other than infinity, the degeneracy in  ${}^1\hat{\rho}$  is broken, and there is a unique set of natural orbitals, which are nearly the canonical orbitals. However, one can show that the atomic-like functions are more relevant for describing the extent of the diradical character at all distances, under our definition.

The phase of the configuration interaction in the right-hand side of eq 7 is also important for correlation; however, the same  ${}^1\hat{\rho}$  could result from the wavefunction in eq 7 or a wavefunction



**Figure 3.** Diradicalism of three different wavefunctions for toy-basis  $\text{Li}_2$  [solid line = FCI energy in arbitrary units]. The PP-CCD wavefunction is similar in diradicalism to the FCI wavefunction, except that the curve is shifted upward. PP-CCD atoms dissociate to perfect monoradical subunits because of less atomic (dynamic) correlation. The UHF wavefunction starts closed-shell and breaks symmetry dramatically.

where this phase is flipped, as in eq 17. In eq 17, no orbital

$$\frac{|1s_A\downarrow 1s_A\uparrow\rangle + |1s_B\downarrow 1s_B\uparrow\rangle}{\sqrt{2}} = \frac{|1\sigma\downarrow 1\sigma\uparrow\rangle + |1\sigma^*\downarrow 1\sigma^*\uparrow\rangle}{\sqrt{2}} \quad (17)$$

(atomic or canonical) is ever singly occupied. In eq 7, the electrons are correlated to maximize the distance between one another ( $\hat{r}_{12}$ ), whereas in eq 17, this distance is minimized, which would be unphysical for the ground state.  $R_2$  will distinguish between these two wavefunctions.  ${}^1\hat{\rho}$ , however, cannot technically differentiate between these two phenomena, although LUMO occupation numbers can generally be assumed to originate from physically reasonable correlations ( $-1 < t < 0$  for PP-CCD amplitudes), allowing  ${}^1\hat{\rho}$ , and also  $\hat{D}$ , to provide some information about the extent and spatial domain of radical behavior; this assumption may only be valid for ground states, however.

**4.3. Diradical Character: Results.** In Figure 3, the diradical character  $R_2$  of  $\text{Li}_2$  is plotted as a function of nuclear separation, using a toy basis consisting of the three s orbitals from the 6-31G set for each atom. The  $R_2$  curve is for the FCI ground-state wavefunction in the singlet space; the shape of the energy curve is also plotted for reference.

The diradical character of a molecule should be viewed as relative to the diradical character that one would expect from a closed-shell system. One-half is then a sort of baseline, because as discussed previously, a closed-shell determinant species has  $R_2 = 0.5$ . (We can also show that closed-shell species have one-quarter triradical and tetradical character, and so on, in inverse powers of two.) For this reason, the percent excess diradicalism, according to our definition, has also been plotted.

$$\% \text{ excess diradicalism} = 2(R_2 - 0.5) \times 100\% \quad (18)$$

Even at very compressed distances,  $\text{Li}_2$  is quite diradical (50.8% at equilibrium) and this converges to nearly 100% at long distances, reflective of the fact that the atoms have almost complete monoradical character, making the combined system a nearly pure diradical. For reference, minimal basis (FCI/STO-3G) singlet  $\text{H}_2$  is 20.8% diradical at equilibrium.

There are also simple formulas to obtain  $R_2$  for unrestricted Hartree–Fock (UHF) and PP-CCD wavefunctions. In eq 19a,  $S$  is the spatial overlap of the least overlapping UHF corresponding orbital pair.<sup>20</sup> In eq 19b,  $t$  refers specifically to  $t_{\text{HH}}^{\text{LL}}$ .

$$\begin{aligned} \text{(a)} \quad R_2^{\text{UHF}} &= 1 - \frac{S^2}{2} \\ \text{(b)} \quad R_2^{\text{PP-CCD}} &= \frac{(1-t)^2}{2(1+t^2)} \end{aligned} \quad (19)$$

In Figure 3, the excess diradicalism associated with the  $R_2$  values of UHF and one-pair PP-CCD wavefunctions are also plotted as functions of  $\text{Li}_2$  bond distance, for comparison with FCI (same basis).

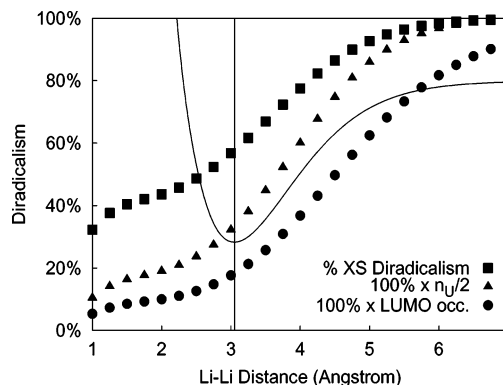
**4.4. Diradical Character: Discussion of Results.** Of primary concern here is the meaning of the radical character values. We have defined a quantity which we call the radical character. However, this is not the same as a theory of radical behavior. Radical character should be some theoretical measure of the similarity in the electronic structure of radicals, whereas radical behavior is that which is typically experimentally observed of such species. Concretely, there has been discussion of molecules such as the  $((i\text{-Pr})_2\text{P})_2(\text{B}(t\text{-Bu}))_2$  ring molecule (BPBP).<sup>17,24</sup> The claim by Scheschkewitz et al.,<sup>24</sup> who first synthesized this molecule, is that it is an indefinitely stable singlet diradical. Although site-specific reactivity is generally indicative of radical character in the electronic structure, this reactivity might be sterically hindered in this particular molecule. We would like to separate out these effects by looking at the electronic structure alone, to assign the molecule a theoretical diradical character.

BPBP is 16.9% “diradicaloid”, according to the perfect-pairing/LUMO analysis<sup>17</sup> ( $100\% \times {}^1\rho_{\text{LL}}$ , where  ${}^1\rho_{\text{LL}}$  is the LUMO occupation) for a 71-pair PP-CCD/6-31G(d) wavefunction.

$${}^1\rho_{\text{LL}}^{\text{PP-CCD}} = \frac{2t^2}{1+t^2} \quad (20)$$

Using eq 19b, we obtain 55.7% excess diradicalism for this wavefunction ( $t = -0.30421$ ), according to our definition. We caution against attaching too much significance to these raw numbers; under either analysis, one would reach the same practical conclusion, that BPBP is about as diradical as  $\text{Li}_2$  is at equilibrium. Concerning the 20.8% excess diradicalism of equilibrium  $\text{H}_2$ , we would not consider this to be a diradical. We would like any theoretical definition to yield vanishing radical character for closed-shell determinants, but we must remember that no real system, including one whose behavior is essentially closed-shell, is described by a single determinant. There is no a priori value that should correspond to a system which behaves closed-shell, and systems with closed-shell behavior may exhibit a range of character values under any definition.

It is reasonable to expect that wavefunctions with radical character will be diagnosed as such under a variety of analyses. The quest is to identify and extract the most fundamental similarity between radicals. Such an analysis should be theoretically satisfying in its interpretation, and it should provide the most robust prediction of radical behavior, when applied to complicated wavefunctions. Figure 4 shows a few proposed measures of diradical character, applied to the one-pair PP-CCD/toy-basis  $\text{Li}_2$  wavefunction. This wavefunction was chosen, because it is easy to analyze with respect to these different measures and it is easy to think about, as it reduces to a 2-in-2 model problem. The percent excess diradicalism as defined here, the percentage of two unpaired electrons ( $n_D/2$ ) achieved according to  $\hat{D}$ , and the percentage of one electron in the LUMO ( ${}^1\rho_{\text{LL}}$ ) have been plotted. This last measure is equivalent, in this



**Figure 4.** Three different measures of diradicalism for toy-basis one-pair PP-CCD  $\text{Li}_2$  [solid line = FCI energy in arbitrary units]. The measures are qualitatively the same, and algebraically related, for this simple case.

case, to the percentage of two unpaired electrons obtained from the proposed modified  $\hat{D}$ .<sup>14</sup> For this simple case, all three values measure the same correlation effect and therefore behave similarly.

For the PP-CCD case, we have the conceptual advantage that the entire LUMO occupancy is a result of double excitation out of the HOMO ( ${}^1\rho_{\text{HH}} = 2 - {}^1\rho_{\text{LL}}$ ), and the core orbitals are exactly doubly occupied. This means that  $n_D$  can be written as function of  ${}^1\rho_{\text{LL}}$  only, and if we assume that  $t \leq 0$ , we can write  $R_2$  as a function of  ${}^1\rho_{\text{LL}}$  as well.

$$\text{(a)} \quad 100\% \times \frac{n_D}{2} = 100\% \times [2({}^1\rho_{\text{LL}}) - ({}^1\rho_{\text{LL}})^2]$$

$$\text{(b)} \quad \% \text{ excess diradicalism } (R_2) = 100\% \times \sqrt{2({}^1\rho_{\text{LL}}) - ({}^1\rho_{\text{LL}})^2} \quad (21)$$

By choosing this form of the wavefunction, the homogeneous mixtures of the HOMO and LUMO are automatically the radical orbitals. All of the quantities,  $R_2$ ,  ${}^1\rho_{\text{LL}}$ , and  $n_D$ , are therefore isomorphic for the 2-in-2 perfect-pairing case, but we believe that  $R_2$  is the fundamentally most meaningful quantity, of which  ${}^1\rho_{\text{LL}}$  and  $n_D$  should be considered indicators. It is the authors' hypothesis that each of these measures should serve as some sort of threshold criteria. Molecules whose diradicalism is above a certain value on one of these scales (which corresponds uniquely to a different threshold value on a different scale) will rapidly begin to behave more diradically as this value increases. We say this, because each measure does indicate the extent to which a molecule has singly occupied orbitals, but we believe that an orbital must be quite singly occupied before it is particularly reactive. This remains to be verified.

In terms of orbital single occupancy, our new definition is the rigorous generalization of extraction of radical character to the non-perfect-pairing case. Our analysis should provide the best orbitals for thinking about diradical (or higher) character, and it will, hopefully, be a more robust method for analyzing more complicated systems.

**4.5. Triradical Character.** Figure 5 shows the triradical character  $R_3$  of linear  $\text{H}_3$  along a symmetric stretch coordinate, done at the FCI/6-31G (two s shells) level in the doublet  $M_S = -1/2$  space. The closed-shell baseline for triradical character is one-quarter, as stated earlier. As one might expect, the triradical character at small distances is nearly one-half (33% excess), because one of the canonical orbitals is almost always singly occupied, and a doubly occupied canonical orbital can be transformed in many ways (reflecting the lack of left-right,

TABLE 1: The Values of  $R_m^{(a)}$  for an FCI/6-31G Be Atom<sup>a</sup>

$m$	$R_m$	$R_m^{(2)}$	$R_m^{(3)}$	$R_m^{(4)}$	$R_m^{(5)}$	$R_m^{(6)}$	$R_m^{(7)}$	$R_m^{(8)}$	$R_m^{(9)}$
1	0.620 972 036 4	0.620 972 032 0	0.50	0.50	0.020	0.020	0.016	0.016	0.0024
2	0.617 707 775 3	0.500 777 968 3	0.016	0.016					
3	0.310 454 260 3	0.008 129 358 3	0.000 080						
4	0.310 454 117 3	0.000 000 227 6							

<sup>a</sup>[ $1 \leq m \leq n$ , and  $a$  ranges from 1 to the maximum allowed by the basis size for a given  $m$ .] There are clear patterns relating lower radical characters to the higher ones, most notably  $R_1 = R_1^{(2)} \approx R_2$ . This means that these monoradical characters result primarily from a two-electron valence correlation, and so, the monoradical characters in this system are good indicators of the diradical character.

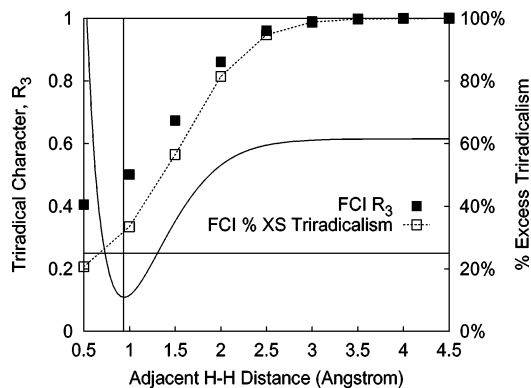


Figure 5. Triradical character for FCI/6-31G symmetric linear  $H_3$  [solid line = FCI energy in arbitrary units].  $H_3$  is 33% triradical at equilibrium and 100% triradical at infinite separation.

in-out, up-down, etc., correlation) to be one-half diradical. At long distance, the radical orbitals are the atomic  $|1s\rangle$  orbitals, and the species becomes completely triradical. This toy system demonstrates that the method functions for higher multiradicals.

**4.6. Approximating Multiradical Character from Monoradical Characters.** We now explore the relationship between higher and lower multiradical characters. Specifically, we focus on the relationship of  $R_2$  to  $R_1$  and  $R_1^{(2)}$ , as defined previously. Simple logical arguments yield the bounds

$$\text{MAX}(0, R_1 + R_1^{(2)} - 1) \leq R_2 \leq R_1 \quad (22)$$

If we know that the highest probability of finding an orbital singly occupied is  $R_1$ , then we cannot have a higher probability of finding two orbitals simultaneously singly occupied (upper bound). Also, if two orthogonal orbitals are found whose probabilities of single occupancy,  $R_1$  and  $R_1^{(2)}$ , respectively, sum to greater than unity, then we know that they must be simultaneously singly occupied some of the time (lower bound). We expect that  $R_2$  will lie between  $R_1 \times R_1^{(2)}$ , when the monoradical single occupancies are uncorrelated, and  $R_1$ , when they are perfectly correlated.

Unless both  $R_1$  and  $R_1^{(2)}$  are near unity, then the bounds in eq 22 are not very tight, so we look for another way to test the possibility that the monoradical characters and diradical characters measure the same correlation effect and that we can use one to approximate the other. In other words, we have the hypothesis, stated previously, that  $R_2 \approx R_1 \approx R_1^{(2)}$  and that  $|\phi_1\rangle^{\text{opt}}$  and  $|\phi_2\rangle^{\text{opt}}$  from the first and second monoradical analyses are the same  $|\phi_1\rangle^{\text{opt}}$  and  $|\phi_2\rangle^{\text{opt}}$  that one would obtain from the full diradical evaluation. The system we choose is the Be atom, done at the FCI/6-31G (one s shell, two sp shells) level. Be was chosen because there are two valence electrons surrounding a nucleus of shielded charge of approximately two, but unlike in a helium atom, these electrons live in a Hilbert space of four

nearly degenerate orbitals, and the interactions of the s and p orbitals in this shell lead to interesting angular correlation.

All of the monoradical through tetradical probabilities of this system are given in Table 1. There are clear patterns in the numbers of this table relating lower radical characters to the higher ones. For example  $R_2 \approx R_1 = R_1^{(2)}$  for the valence correlation, which was our hypothesis. Also  $R_2^{(2)} = R_1^{(3)} = R_1^{(4)} = 0.5$ , which comes from the largely uncorrelated core. Finally  $R_3 = R_4 \approx R_2 \times R_2^{(2)}$ , because slightly correlated diradical characters form the tetradical character, and the triradical character is from the same effect. The remaining unaddressed numbers are from orbitals that have some small occupation due to low-amplitude scatterings. Table 1 is a good illustration of the way that our method isolates a few important correlation effects from a complicated wavefunction.

One finds that the first monoradical orbital is an sp hybridized orbital. There is a two-dimensional submanifold of sp hybrids embedded in the three-dimensional manifold of normalized states in the four-dimensional sp-shell state space; one such state on this sp manifold is converged upon at random in the first monoradical optimization. Now, there is only one sp hybrid remaining on this manifold which is orthogonal to the first one. This orthogonal sp hybrid is the second monoradical orbital, and by symmetry, we have  $R_1^{(2)} = R_1$ , to within numerical noise. These two sp hybrids are members of a two-dimensional manifold of radically degenerate pairs of sp hybrids which could have been converged upon; in each pair, the hybrid partners point in opposite directions from the nucleus.

We also find that the diradical character  $R_2$  is nearly equivalent to these monoradical characters and that the first diradical orbitals are also a pair of sp hybrids pointing in opposite directions. One can easily imagine why this is true. The electrons are correlating such that they have a higher probability of being found alone on opposite sides of the nucleus, even though the aufbau contribution keeps them together in the lower energy  $|2s\rangle$  state most of the time (only 24% excess diradicalism).

One can also imagine that the relationship between monoradical and diradical characters would hold in cases where the first and second monoradical orbitals (the approximate diradical orbital pair) are on more spatially separated sites. A good diagnostic for this assumption is that  $R_1 \approx R_1^{(2)}$ , which should then be approximately  $R_2$ . For FCI/toy-basis  $Li_2$  along the stretch coordinate, the maximum difference between  $R_1$  and  $R_1^{(2)}$  is  $5.4 \times 10^{-5}$  (at 3.25 Å), and the maximum difference between  $R_1$  and  $R_2$  is 0.011 14 (at 5.5 Å).

We are led to wonder whether it is very important that diradical (triradical, etc.) orbitals be simultaneously singly occupied. Perhaps that would be important in concerted electronic mechanisms, but not always. It may be useful to simply establish the values of the largest  $R_1^{(a)}$  and the orbitals to which they belong ( $1 \leq a \leq N$ ). As stated earlier, the



monoradical characters are much cheaper to compute than higher radical characters.

**4.7. Algebraic Connection to  $\hat{D}$  and Perfect Pairing.** The reader may have already noticed that a form similar to  $\hat{D}$  appears in the expression for excess diradicalism for a simple case in eq 21b. There are many ways that one could elaborate on this, and in the interest of space, detailed derivations will not be presented.

Equation 21b holds for a 2-in-2 perfect-pairing system, under the condition that  $t \leq 0$ , which is a reasonable assumption for repulsive correlation. This relationship also holds for the diradical character of each individual pair in a more general PP-CCD wavefunction; because the pairs are noninteracting, each double excitation amplitude for a pair gives us a successive  $R_2^{(a)}$  value. For each pair, we also have  $R_2^{(a)} = R_1^{(2a-1)} = R_1^{(2a)}$ . Putting this all together, we can obtain

$$\sum_{a=1}^N R_1^{(a)} = \frac{n}{2} + \frac{1}{2} \text{Tr}(\hat{D}^{1/2}) \quad (\text{PP-CCD case}) \quad (23)$$

the value of which starts at the one-half baseline for each monoradical orbital with any occupancy and increases with correlation.

Additionally, if one were to define the number of unpaired electrons, we would suggest

$$n_R = \sum_{a=1}^N R_1^{(a)} \quad (24)$$

because this sums over all orbitals, weighted by the probability that an electron is alone in that orbital. First, one sums over those orbitals that can be found to be almost always singly occupied, if there are any, thus obtaining the number of electrons which are almost always alone. Then, there would be a series of orbitals (approximately speaking, mixtures of core and virtual orbitals) which contribute nearly one-half of an electron each, and then come orbitals with only slight occupancy. One can show that for all wavefunctions, the following limits hold

$$0 \leq n_R \leq n \quad (25)$$

and, practically speaking

$$n/2 < n_R < n \quad (26)$$

So, we now have a new expression for the number of unpaired electrons  $n_R$ , using the monoradical characters defined in this work. We can also express  $n_R$  in terms of  $\hat{D}$  for PP-CCD wavefunctions, which are often qualitatively good wavefunctions for thinking about bond breaking and radicals. In this PP-CCD case, the bounds in eqs 25 and 26 are implicitly enforced by the structure imposed on  $|\hat{\rho}\rangle$  by the wavefunction Ansatz; strong pairs contribute nearly two electrons to the total, and weak pairs contribute less. Outside of the perfect-pairing approach,  $n_R$  is still well defined and bounded, but it must be computed by brute force.

A caveat follows: We have only chosen to present eqs 23–25 for the insight they give into  $\hat{D}$ . We cannot recommend that  $n_R$  be used as a measure of radical character. It is not clear what the number of unpaired electrons should mean for radical behavior. Tracing over  $\hat{D}$  or  $\hat{D}^{1/2}$  sums over all correlations, including small amplitude dynamic ones. While dynamic correlation may increase the average aloneness of electrons, it still may not produce a single reactive radical orbital. It has

been pointed out<sup>14</sup> that the derivative of  $n_D$  with respect to small deviations from zero or two in a natural orbital occupation is two, so that the most heavily weighted component of  $n_D$  arises from dynamic correlation. This effect would be exacerbated in  $n_R$ , where that slope is divergent.

Per the discussions in this paper, it seems most relevant to isolate a few primary correlation effects (static correlation). Static correlation could be viewed as a generalized form of symmetry breaking, because in the extreme case, the proper symmetric ground state is a superposition of a few degenerate, symmetry-broken solutions, which are, themselves, nearly eigenstates; this leads to slow dynamics of the system when perturbed along these wavefunction coordinates (static). The effect of static correlation, as interpreted here, is that it leaves electrons to occupy some orbitals mostly alone, as a means of staying away from one another much of the time. The optimization procedure defined herein extracts the best description of these static effects, independent of the particular basis rotation in which the energy is computed or the structure of electron correlation in that basis.

**4.8. Behavior in the Limiting Case of  $n_D$ .** As kindly suggested by one of the referees, we should also address the behavior of our procedure for wavefunctions in which the value of  $n_D$  approaches the  $2n$  limit discussed previously. We start by restating a point made in a recent letter<sup>25</sup> that this limiting case is not likely to be realized in chemically relevant situations. Nonetheless, this concern needs to be addressed to fulfill the stated “satisfying interpretation” and “robustness” criteria. These wavefunctions will be called the highly correlated case, because as addressed earlier,<sup>12</sup> this case occurs when all of the natural orbital occupations are very small.

Because diagonalizing the spinless one-particle density matrix should produce as some of its eigenvectors those orbitals with the largest occupancy, no one-particle state can be found that has significant single or double occupancy in the highly correlated case. This means that the value of  $R_1$  for these systems will be small, and all of the higher  $R_m$  values will be smaller, as  $R_{m+1} \leq R_m$ , always.

We would not consider such a highly correlated system to be a monoradical; it does not contain a single one-particle state that would, by our interpretation, constitute a reactive radical orbital. The utility of the proposed measures of diradical and higher characters is to isolate a dominant correlation which has the effect of leaving electrons alone in orbitals; no single such correlation is present in this case. While we concede that for those cases where  $n_D \approx 2n$ , all  $R_m$  are nearly zero, making them of little use, we are satisfied with this result, because the effects which we are looking for are, in fact, not there. We remind the reader that the motivation was to develop a universally applicable, quantum mechanical analogue to the simple concept of a radical, born out of Lewis pair theory, to explain valency and reactivity.

That said, we draw attention to two cases in which our procedure produces a useful result where  $n_D$  fails. First, we note the behavior of our theory in one subcase of the highly correlated case, when those orbitals that do have some occupancy are far more likely to be singly occupied than doubly occupied. By virtue of summing over all orbitals, we obtain  $n_R \approx n$  (eq 23 does not apply in this case.), indicating that all electrons are unpaired; this value is lowered by any pairing that occurs. Second, we note a more physically relevant situation, where the unphysical limit of  $n_D$  shows consequences outside of the highly correlated case. In another recent letter,<sup>26</sup>  $n_D$  was computed for FCI/aug-cc-pV4Z triplet He.  $n_D$  has a lower bound

of 2 in this case; the computed result is that He has 2.0015 unpaired electrons according to this method. Our number of unpaired electrons,  $n_R$ , cannot exceed the total number of 2 electrons, and the diradical character,  $R_2$ , cannot exceed unity.

In the absolute (unphysical) limit, our  $R_m$  and  $n_R$  values are correct; that is, they are true to the qualities we are trying to quantify. In realistic cases, we are able to recover meaningful results where  $\hat{D}$  fails.

## 5. Conclusion

We have proposed a measure of general multiradical character as a logical extension of the concepts which drive a single-determinant model chemistry, where a radical is well-defined. We have justified this extension based on simple arguments about pairing and reactivity. This definition of radical character provides us with both scalar measures, the  $R_m$ , and with distribution quantities, the radical orbitals, that indicate the extent and spatial domain of this character, respectively. The  $R_m$  values obey reasonable bounds, and they can be interpreted in terms of well-defined probabilities. For perfect-pairing systems, we recover an expression for an  $n_R$  value in terms of  $\hat{D}$ , bringing some insight into the meaning of  $\hat{D}$ . The definition is very general, applicable to wavefunctions of any structure, ground state or otherwise. It can be systematically generalized to an arbitrary degree of radical behavior. Computation of the monoradical character appears to be practical for moderate systems, and reasonably good approximations to diradical and higher characters appear to be possible.

**Acknowledgment.** The following people are thanked for their helpful discussions on this subject and/or critical readings of the manuscript: Andreas Dreuw, Luis Seijo, Matthew Nee, Alán Aspuru-Guzik, John Herbert, and most notably, Garnet Chan, Gregory Beran, and Joseph Subotnik. The encouragement of family and many friends was appreciated (A. D. D.). We gratefully acknowledge funding from the Director of the Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy, under contract DE-AC03-76SF0098.

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