Evaluation of S2 in restricted, unrestricted Hartree–Fock, and density functional based theories

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Evaluation of $\langle S^2 \rangle$ in restricted, unrestricted Hartree−Fock, and density functional based theories

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A simple formalism for the evaluation of $\langle S^2 \rangle$ in terms of the two-particle density matrix is presented. The implementation of the formalism in the restricted open-shell Hartree–Fock (ROHF), unrestricted HF (UHF) and density functional (DFT) based theories is discussed. Rules governing the nonzero S^2 matrix elements in the UHF based methods are presented. Further examples are given of $\langle S^2 \rangle$ in several atomic and radical systems from very simple density functional models. © *1995 American Institute of Physics.*

I. INTRODUCTION

The expectation value of the total spin angular momentum, $\langle S^2 \rangle$, is a very important indicator for the quality of theoretical treatments of open-shell systems. The deviation of this expectation value from the exact value is commonly used as a quantitative measure of spin contamination in an approximate wave function. For a single Slater-determinant UHF wave function, the evaluation of $\langle S^2 \rangle$ is straightforward. For correlated wave functions, Purvis *et al.*[1] have discussed the computation of $\langle S^2 \rangle$ for coupled cluster wave functions. But their formula did not take into account the spin perturbation, as pointed out by Chen and Schlegel.[2] Cassam-Chenaï and Chandler[3] investigated the total spin angular momentum of an unrestricted complete active space self-consistent-field (UCASSCF) wave function. More recently, Chen and Schlegel[2] reported a computational scheme for $\langle S^2 \rangle$ for a variety of correlated wave functions. They also tabulated explicit relations for the nonzero matrix elements. Unfortunately, these relations are quite complicated and some are redundant.

S^2 is a typical two-particle property. It would be more convenient to calculate its expectation value under the framework of the two-particle density matrix. Also, a formula based on the density matrix is expected to work in general situations.

Another question we want to address here is the evaluation of $\langle S^2 \rangle$ in density functional theory. Earlier studies of $\langle S^2 \rangle$ in DFT[4,5] were carried out by employing an unrestricted determinantal wave function constructed from the occupied Kohn–Sham orbitals. The values so obtained are not those of the interacting (real) system but rather of the noninteracting reference (fictitious) system with the same charge density. The authors[4] noted that they were unable to calculate $\langle S^2 \rangle$ for interacting systems.

As mentioned earlier, the total spin angular momentum is two particle in nature, and in order to calculate it in DFT, a relationship to the density has to be established first. In this Communication, we shall examine two simple models and present some preliminary results.

II. FORMALISM FOR $\langle S^2 \rangle$

Almost four decades ago, Löwdin[6] has shown that the total spin for an N-electron system is

$$\langle S^2 \rangle = -\frac{N(N-4)}{4} + \int \Gamma(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2 | \mathbf{r}_1 s_2, \mathbf{r}_2 s_1) d\mathbf{x}_1 \, d\mathbf{x}_2, \quad (1)$$

where $\mathbf{x}_i = (\mathbf{r}, \sigma_i)$ is the combined spatial ($\mathbf{r}_i$) and spin (σ_i) coordinate of electron i and $\Gamma(\mathbf{x}_1', \mathbf{x}_2' | \mathbf{x}_1, \mathbf{x}_2)$ is the two-particle density matrix and is normalized to $N(N-1)/2$,

$$\Gamma(\mathbf{x}_1', \mathbf{x}_2' | \mathbf{x}_1, \mathbf{x}_2)$$
$$= \frac{N(N-1)}{2} \int \Psi^*(\mathbf{x}_1', \dots, \mathbf{x}_N') \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) d\mathbf{x}_3, \dots, d\mathbf{x}_N. \quad (2)$$

Judging from Eq. (1), we conclude that the calculation of $\langle S^2 \rangle$ requires both diagonal and off-diagonal elements of the two-particle density matrix. This point will be more transparent by rewriting Eq. (1) as

$$\langle S^2 \rangle = \frac{-N(N-4)}{4} + \int [\Gamma^{\alpha\alpha\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2)$$
$$+ \Gamma^{\beta\beta\beta\beta}(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2) + \Gamma^{\alpha\beta\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2)$$
$$+ \Gamma^{\beta\alpha\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2)] d\mathbf{r}_1 \, d\mathbf{r}_2. \quad (3)$$

The superscripts in Eq. (3) indicate the spin components of the two-particle density matrix. The first two terms are diagonal elements. They are commonly known as pair densities with the α and β spins and normalized to $N_\alpha(N_\alpha - 1)/2$ and $N_\beta(N_\beta - 1)/2$, respectively. Here N_α and N_β indicates the number of α and β electrons in the system. $N = N_\alpha + N_\beta$ and we assume $N_\alpha \geq N_\beta$.

The other two terms in Eq. (3) are off-diagonal elements (in spin coordinates) and are equal according to the symmetry properties of the two-particle density matrix. We then obtain

$$\langle S^2 \rangle = -N(N-4)/4 + N_\alpha(N_\alpha - 1)/2 + N_\beta(N_\beta - 1)/2$$
$$+ \int [\Gamma^{\alpha\beta\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2)$$
$$+ \Gamma^{\beta\alpha\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2)] d\mathbf{r}_1 \, d\mathbf{r}_2$$
$$= \frac{N_\alpha - N_\beta}{2} \left(\frac{N_\alpha - N_\beta}{2} + 1 \right) + N_\beta$$
$$+ 2 \int \Gamma^{\alpha\beta\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 \, d\mathbf{r}_2. \quad (4)$$

It is clear that the calculation of $\langle S^2 \rangle$ requires the integral over the off-diagonal two-particle density matrix. Since we are concerned about a pure spin state in the principal case $(S = M_S)$ and $M_S = (N_\alpha - N_\beta)/2$, it is evident that the first term from Eq. (4) is the exact value for $\langle S^2 \rangle$. Therefore, the spin contamination, if it occurs, indicates the incomplete cancellation of the last two terms.

In the following sections, we will find the representation of the integrand in Eq. (4) and the computation of the integrals with different wave functions or density functionals.

III. $\langle S^2 \rangle$ IN ROHF BASED THEORIES

We start with the ROHF based methods, which include ROHF itself and configuration interaction (CI) wave functions based on the ROHF orbitals. The wave function for an open-shell system can be written, in general, as

$$\Psi = \sum_i c_i \Phi_i, \tag{5}$$

and

$$\Phi = \frac{1}{\sqrt{N!}} |\phi_1(1)\alpha, \dots, \phi_{N_\alpha}(N_\alpha)\alpha, \psi_1(1)\beta, \dots, \psi_{N_\beta}(N_\beta)\beta|, \tag{6}$$

where c_i are the CI expansion coefficients. The Φ are Slater determinants arising from N_α occupied α orbitals $\{\phi\}$, and N_β occupied β orbitals $\{\psi\}$.

In the ROHF based treatments, the α and β spin orbitals share the same spatial parts, i.e., the $\{\phi\}$ and $\{\psi\}$ are the same sets of orthonormal orbitals. For there to be a nonzero value of $\Gamma^{\alpha\beta\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2)$, two Slater determinants can differ, at most, by two orbitals. Furthermore, since the integrand is *diagonal* in terms of spatial coordinates and the orbitals are orthonormal, a nonzero integral over $\Gamma^{\alpha\beta\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2)$ only results from identical Slater determinants. And for each single Slater determinant, its contribution to the integral over $\Gamma^{\alpha\beta\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2)$ is $-N_\beta/2$. Therefore, for a ROHF wave function, the last two terms in Eq. (4) cancel exactly and the wave function describes a pure spin state. For CI wave functions, each Slater determinate contributes to the integral with a value of $-N_\beta/2$, and the total integral is simply $-\sum_i c_i^2 N_\beta/2 = -N_\beta/2$. Again, the cancellation is complete and the CI wave function in this case is not spin contaminated. In conclusion, the ROHF and CI treatments based on the ROHF orbitals are spin contamination free methods.

IV. $\langle S^2 \rangle$ in UHF based theories

If we use the UHF itself or a CI method based on the UHF spin orbitals, the situation is complicated due to nonorthogonality between the α and β sets of orbitals. Even though the integrand $\Gamma^{\alpha\beta\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2)$ still vanishes when two Slater determinants differ by more than two orbitals, the integral is no longer restricted to contributions from identical Slater determinants only. Two Slater determinants, as long as they have nonzero values for the integrand, contribute, in principle, to the final integral. In the following, we briefly summarize the rules for a nonzero integrand.

Case 1: Between identical Slater determinants:

$$\Gamma^{\alpha\beta\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2),$$

$$= -\frac{1}{2} \sum_{i \in \alpha}^{\text{occ}} \phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_2) \sum_{j \in \beta}^{\text{occ}} \psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_1). \tag{7}$$

Then the integral in Eq. (4) is

$$\int \Gamma^{\alpha\beta\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1\,d\mathbf{r}_2$$

$$= -\frac{1}{2} \int \sum_{i \in \alpha}^{\text{occ}} \phi_i^*(\mathbf{r}_1)\phi_i(\mathbf{r}_2) \sum_{j \in \beta}^{\text{occ}} \psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_1)d\mathbf{r}_1\,d\mathbf{r}_2,$$

$$= -\frac{1}{2} \sum_{i \in \alpha}^{\text{occ}} \sum_{j \in \beta}^{\text{occ}} \left| \int \phi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1)d\mathbf{r}_1 \right|^2. \tag{8}$$

Case 2: Between two Slater determinants differing by a single α orbital $\phi_k \to \phi_l$:

$$\Gamma^{\alpha\beta\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2)$$

$$= -\frac{1}{2}(-1)^{p_k + p_l}\phi_k^*(\mathbf{r}_1)\phi_l(\mathbf{r}_2) \sum_{j \in \beta}^{\text{occ}} \psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_1), \tag{9}$$

where p_i refers to the sequential number of the orbital i in the concerned Slater determinant. Similar formulas exist when two Slater determinants differ by one β orbital.

Case 3: Between two Slater determinants differing by a single α orbital $\phi_i \to \phi_k$ and a single β orbital $\psi_j \to \psi_l$:

$$\Gamma^{\alpha\beta\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2)$$

$$= -\frac{1}{2}(-1)^{p_i + p_j + p_k + p_l}\phi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\psi_l(\mathbf{r}_1)\phi_k(\mathbf{r}_2). \tag{10}$$

Note that two Slater determinants differing by either two α or two β orbitals do not contribute to the integrand.

After the integrand is found, the integral is just the product of two overlaps of the α and β orbitals involved. The total integral requires the CI coefficients and the overlap matrix between the α and β sets of orbitals. The latter can be quickly calculated and stored beforehand. Therefore, the calculation of $\langle S^2 \rangle$ with UHF based correlated wave functions will not be too much more expensive than in the ROHF case.

V. $\langle S^2 \rangle$ IN DENSITY FUNCTIONAL THEORY

In DFT, the properties, either of one-particle nature or of two-particle nature, are written as functionals of ρ^α and ρ^β. Most of these functionals are just approximate, since the exact ones are not known. We discuss $\langle S^2 \rangle$ for two simple approximations in the following.

With the single Slater determinant as the wave function, Löwdin has shown[7] that the two-particle density matrix can be expressed in terms of one-particle density matrices as follows:

$$\Gamma(\mathbf{x}_1',\mathbf{x}_2'|\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{2}[\gamma(\mathbf{x}_1'|\mathbf{x}_1)\gamma(\mathbf{x}_2'|\mathbf{x}_2)$$
$$- \gamma(\mathbf{x}_1'|\mathbf{x}_2)\gamma(\mathbf{x}_2'|\mathbf{x}_1)]. \tag{11}$$

For a more general wave function, including the exact one, we may expand its two-particle density matrix in terms of its one-particle density matrices, i.e.,

$$\Gamma(\mathbf{x}_1',\mathbf{x}_2'|\mathbf{x}_1,\mathbf{x}_2) = \tfrac{1}{2}[\gamma(\mathbf{x}_1'|\mathbf{x}_1)\gamma(\mathbf{x}_2'|\mathbf{x}_2) - \gamma(\mathbf{x}_1'|\mathbf{x}_2)\gamma(\mathbf{x}_2'|\mathbf{x}_1)]$$

$$+ \mathscr{G}(\mathbf{x}_1',\mathbf{x}_2'|\mathbf{x}_1,\mathbf{x}_2), \tag{12}$$

where $\mathscr{G}(\mathbf{x}_1',\mathbf{x}_2'|\mathbf{x}_1,\mathbf{x}_2)$ is a small modification term with norm zero. For a first approximation, we drop this $\mathscr{G}$ function from Eq. (12). We then obtain the following relations:

$$\Gamma^{\alpha\alpha\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2) = P_2^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)$$

$$= [\rho^\alpha(\mathbf{r}_1)\rho^\alpha(\mathbf{r}_2) - \gamma^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)^2]/2, \tag{13}$$

$$\Gamma^{\beta\beta\beta\beta}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2) = P_2^{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2)$$

$$= [\rho^\beta(\mathbf{r}_1)\rho^\beta(\mathbf{r}_2) - \gamma^{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2)^2]/2, \tag{14}$$

$$\Gamma^{\alpha\beta\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2) = \gamma^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)\gamma^{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2)/2, \tag{15}$$

where $\rho^\sigma(\mathbf{r}_i) = \gamma^{\sigma\sigma}(\mathbf{r}_i|\mathbf{r}_i)$.

By using Eqs. (13)–(15), we can easily find the integrand in Eq. (4) to be

$$\Gamma^{\alpha\beta\beta\alpha}(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1,\mathbf{r}_2) = -\tfrac{1}{2}[\rho^\alpha(\mathbf{r}_1)\rho^\alpha(\mathbf{r}_2)$$

$$-2P_2^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)]^{1/2}[\rho^\beta(\mathbf{r}_1)$$

$$\times \rho^\beta(\mathbf{r}_2) - 2P_2^{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2)]^{1/2}. \tag{16}$$

Therefore,

$$\langle S^2 \rangle = \frac{N_\alpha - N_\beta}{2}\left(\frac{N_\alpha - N_\beta}{2} + 1\right) + N_\beta - \int [\rho^\alpha(\mathbf{r}_1)\rho^\alpha(\mathbf{r}_2)$$

$$-2P_2^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)]^{1/2}[\rho^\beta(\mathbf{r}_1)\rho^\beta(\mathbf{r}_2)$$

$$-2P_2^{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2)]^{1/2} \, d\mathbf{r}_1 d\mathbf{r}_2. \tag{17}$$

It is easy to verify that Eq. (17) gives the exact result of $\langle S^2 \rangle$ for closed-shell systems.

Now, let us introduce the following correlation hole function:

$$-h^{\sigma\sigma'}(\mathbf{r}_1,\mathbf{r}_2) = \frac{2P_2^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)}{\rho^\sigma(\mathbf{r}_1)} - \rho^{\sigma'}(\mathbf{r}_2). \tag{18}$$

Equation (17) can be simplified further:

$$\langle S^2 \rangle = \frac{N_\alpha - N_\beta}{2}\left(\frac{N_\alpha - N_\beta}{2} + 1\right) + N_\beta$$

$$- \int [h^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2)\rho^\alpha(\mathbf{r}_1)]^{1/2}$$

$$\times [h^{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2)\rho^\beta(\mathbf{r}_1)]^{1/2} \, d\mathbf{r}_1 \, d\mathbf{r}_2. \tag{19}$$

In the following, two simple models for the functionals of $h^{\sigma\sigma}$ are examined. Note that only the exchange part of the correlation hole function is considered here.

In the first model, the hole function is chosen to be a Gaussian function with the proper normalization, i.e.,

$$h_X^{\sigma\sigma}(\mathbf{r}_1,s) = \rho^\sigma(\mathbf{r}_1)\exp(-\zeta_\sigma s^2) \tag{20}$$

and

$$4\pi \int h_X^{\sigma\sigma}(\mathbf{r}_1,s)s^2 \, ds = 1. \tag{21}$$

These lead to

TABLE I. $\langle S^2 \rangle$ from three models based on numerical DFT calculations.

Systems	$\langle S^2 \rangle$			
	Gaussian	LSD	Noninteracting	Exact
Li(^2S)	0.715 11	0.750 13	0.750 00	0.75
Na(^2S)	0.670 74	0.750 62	0.750 06	0.75
B(^2P)	0.449 85	0.758 89	0.751 71	0.75
Al(^2P)	0.481 91	0.761 20	0.751 75	0.75
F(^2P)	0.382 20	0.768 13	0.751 43	0.75
Cl(^2P)	0.387 88	0.770 76	0.751 67	0.75
Cu(^2S)	0.463 93	0.785 63	0.751 68	0.75
C(^3P)	1.446 40	2.001 91	2.002 58	2.00
Si(^3P)	1.488 15	2.003 27	2.001 66	2.00
O(^3P)	1.370 65	2.011 84	2.003 98	2.00
S(^3P)	1.381 98	2.009 28	2.002 56	2.00
N(^4S)	2.987 65	3.750 00	3.753 23	3.75
P(^4S)	3.020 43	3.750 38	3.750 62	3.75
Cr(^7S)	10.4842	12.00 01	12.00 01	12.0
CH$_3$($^2A_2''$)	0.425 18	0.786 69	0.752 39	0.75
CH$_2$($^3\Sigma_g^-$)	1.483 78	2.017 26	2.004 79	2.00
O$_2$($^3\Sigma_g^-$)	1.174 19	2.016 30	2.003 85	2.00

$$\zeta_\sigma = \pi\rho^\sigma(\mathbf{r}_1)^{2/3}. \tag{22}$$

Therefore, the total spin angular momentum for this model is

$$\langle S^2 \rangle = \frac{N_\alpha - N_\beta}{2}\left(\frac{N_\alpha - N_\beta}{2} + 1\right) + N_\beta - 4\pi \int \rho^\alpha(\mathbf{r}_1)$$

$$\times \rho^\beta(\mathbf{r}_1)d\mathbf{r}_1 \int \exp\left(\frac{-(\zeta_\alpha + \zeta_\beta)s^2}{2}\right)s^2 \, ds$$

$$= \frac{N_\alpha - N_\beta}{2}\left(\frac{N_\alpha - N_\beta}{2} + 1\right) + N_\beta - \int \rho^\beta(\mathbf{r}_1)$$

$$\times \left(\frac{2}{1 + (\rho^\beta(\mathbf{r}_1)/\rho^\alpha(\mathbf{r}_1))^{2/3}}\right)^{3/2} \, d\mathbf{r}_1. \tag{23}$$

From Eq. (23), we immediately see that for $\langle S^2 \rangle$ to be equal to the exact value, the integral part should equal to the total number of β electrons in the system N_β. This can be possibly achieved in two general cases. The first corresponds to $\rho^\alpha(\mathbf{r}_1) = \rho^\beta(\mathbf{r}_1)$ for all $\mathbf{r}_1$, which is true for closed-shell systems. Another case appears when spin polarization happens, i.e., there are both regions of positive $(\rho^\alpha > \rho^\beta)$ and of negative $(\rho^\alpha < \rho^\beta)$ spin distributions. For wave functions of a single-Slater determinant from the ROHF treatment, $\rho^\alpha \geqslant \rho^\beta$ everywhere, and therefore $\langle S^2 \rangle$, calculated from Eq. (23), should be smaller than the exact value. This is true, as revealed from the data shown in Table I. These results are obtained at the experimental geometries with the fully numerical DFT package NUMOL.[8,9]

The second model examined is based on a homogeneous electron gas. The exchange part of the correlation hole function is represented by the following spherically symmetric function:[10]

$$h_X^{\sigma\sigma}(\mathbf{r}_1,s) = 9\rho^\alpha(\mathbf{r}_1)j_1^2(k_F^\sigma s)/(k_F^\sigma s)^2, \tag{24}$$

where $j_1(x)$ is the first-order spherical Bessel function and is given by $j_1(x) = \sin x/x^2 - \cos(x)/x$ and k_F^σ is the Fermi momentum specified by $k_F^\sigma = [6\pi^2\rho^\sigma(\mathbf{r}_1)]^{1/3}$. With this functional, $\langle S^2 \rangle$ is found to be

$$\langle S^2 \rangle = \frac{N_\alpha - N_\beta}{2}\left(\frac{N_\alpha - N_\beta}{2} + 1\right) + N_\beta$$
$$- 36\pi \int \rho^\alpha(\mathbf{r}_1)\rho^\beta(\mathbf{r}_1)d\mathbf{r}_1 \int \frac{j_1(k_F^\alpha s)j_1(k_F^\beta s)}{k_F^\alpha k_F^\beta}\, ds. \tag{25}$$

The integration over the product of two spherical Bessel functions is[11]

$$\int_0^\infty j_1(ax)j_1(bx)dx = \frac{\pi}{2\sqrt{ab}}\int_0^\infty x^{-1}J_{3/2}(ax)J_{3/2}(bx)dx$$
$$= \begin{cases} \pi b/(6a^2), & 0 < b \leqslant a, \\ \pi a/(6b^2), & a < b < \infty. \end{cases} \tag{26}$$

By inserting Eq. (26) into Eq. (25), we have

$$\langle S^2 \rangle = \frac{N_\alpha - N_\beta}{2}\left(\frac{N_\alpha - N_\beta}{2} + 1\right) + N_\beta$$
$$- \int \rho^\sigma(\mathbf{r}_1)d\mathbf{r}_1 \begin{cases} \sigma = \alpha, & \text{if } \rho^\alpha(\mathbf{r}_1) \leqslant \rho^\beta(\mathbf{r}_1), \\ \sigma = \beta, & \text{if } \rho^\alpha(\mathbf{r}_1) > \rho^\beta(\mathbf{r}_1), \end{cases}$$
$$= \frac{N_\alpha - N_\beta}{2}\left(\frac{N_\alpha - N_\beta}{2} + 1\right) - \int_{\rho^s < 0} \rho^s(\mathbf{r}_1)d\mathbf{r}_1, \tag{27}$$

where the spin density $\rho^s(\mathbf{r}_1) = \rho^\alpha(\mathbf{r}_1) - \rho^\beta(\mathbf{r}_1)$.

The above relation indicates that the spin contamination arises from the negative spin regions. Evidently, there will be no contamination if $\rho^\alpha \geqslant \rho^\beta$ holds true over the entire space, as in the case of the ROHF treatment. Otherwise the integral will return a negative value and the $\langle S^2 \rangle$ will be larger than the exact. The expectation values of S^2 in a few elements and radicals are tabulated in Table I under the LSD column.

At this point, it would be interesting to compare the density functional hole model results with those from the Slater determinant constructed from the occupied Kohn–Sham orbitals. Before we go further, let us stress that the Kohn–Sham Slater determinant is *not* the wave function of the interacting (real) system. It represents a fictitious noninteracting reference system with the same charge density as the real system. Furthermore, for systems with nonzero spin density (magnetization density), one requires a different noninteracting (Kohn–Sham) potential for each of the α and β spins in order to reproduce ρ^α and ρ^β. Its usage here is intended to be exploratory, and whether this approach should be encouraged or not requires further investigation. When one treats the Slater determinant for the noninteracting reference system as the wave function for the interacting system, the correlation hole functions are[12]

$$h^{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)\rho^\sigma(\mathbf{r}_1) = \gamma^{\sigma\sigma}(\mathbf{r}_1,\mathbf{r}_2)^2, \tag{28}$$

where $\gamma^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{i\in\alpha}^{\text{occ}}\psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_2)$ and $\gamma^{\beta\beta}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{j\in\beta}^{\text{occ}}\phi_j^*(\mathbf{r}_1)\phi_j(\mathbf{r}_2)$, with $\{\psi_i(\mathbf{r})\}$ for α and $\{\phi_j(\mathbf{r})\}$ for β Kohn–Sham spin orbitals.

The total spin angular momentum is given by

$$\langle S^2 \rangle = \frac{N_\alpha - N_\beta}{2}\left(\frac{N_\alpha - N_\beta}{2} + 1\right) + N_\beta$$

$$- \sum_{i\in\alpha}^{\text{occ}}\sum_{j\in\beta}^{\text{occ}}\left|\int \psi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)d\mathbf{r}_1\right|^2, \tag{29}$$

$$\geqslant \frac{N_\alpha - N_\beta}{2}\left(\frac{N_\alpha - N_\beta}{2} + 1\right) + N_\beta$$

$$- \sum_{j\in\beta}^{\text{occ}}\sum_{i\in\alpha}^{\infty}\left|\int \psi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)d\mathbf{r}_1\right|^2,$$

$$= \frac{N_\alpha - N_\beta}{2}\left(\frac{N_\alpha - N_\beta}{2} + 1\right). \tag{30}$$

Again, the expectation value of S^2 has the exact value as the lower bound.

Equation (29) has been employed to calculate $\langle S^2 \rangle$, and the results are shown in Table I under the column of "noninteracting."

These three different models, all in the framework of DFT, can have their performance on the $\langle S^2 \rangle$ calculation checked by comparison with the exact value. The Gaussian model always produces smaller expectation values. For the other two, the $\langle S^2 \rangle$ are slightly larger than the exact ones. We believe that the LSD model, a strictly density functional model, should serve as a very good starting model for further improvement.

VI. FINAL REMARKS

We have given a simple formula for the calculation of $\langle S^2 \rangle$. The formula depends on the integral of a single component of the two-particle density matrix. The scheme to evaluate such an integral in ROHF and UHF based theories are discussed. The three rules, which govern all the nonzero matrix elements in the UHF based methods, can easily be implemented in the current quantum chemistry packages. We also discussed the treatment of $\langle S^2 \rangle$ in the framework of density functional theory. The preliminary results show encouraging signs for further studies in this direction.

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