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First principles method for the calculation of zero-field splitting tensors in periodic systems

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A formalism for the evaluation of zero-field splitting tensors using Kohn-Sham orbitals obtained from periodic density functional calculations is presented. Details for calculations involving all occupied states and integration over the Brillouin zone are included. Numerically intensive and difficult six-dimensional integration in real space is avoided by calculating all quantities in reciprocal space, leading to a considerably more efficient and stable scheme.

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I. INTRODUCTION

Density functional theory (DFT) using the Kohn-Sham scheme[1,2] has become one of the most widely used tools in modern *ab initio* electronic-structure calculations. Here we present an efficient method for the calculation of the first-order (spin-spin) contribution to the zero-field splitting tensor, which arises in *high-spin* ($S \geqslant 1$) defect centers, using Kohn-Sham orbitals obtained from periodic spin-polarized calculations. We restrict ourselves to the presentation of the mathematical formalism and computational procedure, as results using, and discussions regarding, this approach have appeared elsewhere.[3–7]

The zero-field splitting tensor (D tensor) is often measured in electron spin resonance (ESR) experiments.[8–12] Reliable calculation of the zero-field splitting tensor coupled with other derived quantities from *ab initio* calculations provides a useful tool in the assignment of the microscopic structure of high-spin defect centers.

The results of ESR experiments are conventionally quoted in terms of spin Hamiltonian parameters, which essentially allow for the description of an effect with only a few parameters. In the case of the spin-spin interaction this quantity is usually written $H_{ss} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$ where $\mathbf{D}$ is the D tensor and $\mathbf{S}$ is the total effective spin of the system. The origin of this can be seen by considering the simplest case of two electrons. The energy of the magnetic dipole moment between electrons 1 and 2 is given by

$$H_{ss} = \frac{g_e^2 \mu_B^2}{r^5}[(\mathbf{s}_1 \cdot \mathbf{s}_2) r^2 - 3(\mathbf{s}_1 \cdot \mathbf{r})(\mathbf{s}_2 \cdot \mathbf{r})], \qquad (1)$$

where $\mathbf{r}$ is the vector between the electrons, g_e is the Landé splitting factor, and μ_B is the Bohr magneton. The spatial and spin components can be separated to arrive at the familiar form quoted in ESR literature in terms of the effective total spin $\mathbf{S} = \Sigma_i \mathbf{s}_i$ by a change of *basis* from the individual spin operators to the total effective spin. In the Cartesian representation, the result is[13]

$$H_{ss} = \frac{1}{2}\mathbf{S}^T \begin{bmatrix} \left\langle \frac{r^2 - 3x^2}{r^5} \right\rangle & \left\langle \frac{-3xy}{r^5} \right\rangle & \left\langle \frac{-3xz}{r^5} \right\rangle \\ & \left\langle \frac{r^2 - 3y^2}{r^5} \right\rangle & \left\langle \frac{-3yz}{r^5} \right\rangle \\ & & \left\langle \frac{r^2 - 3z^2}{r^5} \right\rangle \end{bmatrix} \mathbf{S}. \qquad (2)$$

For a more detailed account of the theory of electron spin resonance, see Refs. 14–16.

We first give the formalism for the two-particle system in detail. Then the generalization of this fundamental procedure is made to the inclusion of all valence states and integration over the Brillouin zone.

II. FORMALISM

A. Two-particle system

For the two-particle system, the integral we are interested in may be written

$$I_{ab} = \frac{1}{2} \int \int \rho(\mathbf{r}_1, \mathbf{r}_2) f_{ab}(\mathbf{r}_1 - \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \qquad (3)$$

where $f_{ab}(\mathbf{r}_1 - \mathbf{r}_2)$ may be written in terms of a single variable $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ as

$$f_{ab}(\mathbf{r}) = \frac{r^2 \delta_{ab} - 3(\mathbf{r})_a (\mathbf{r})_b}{r^5}, \qquad (4)$$

and a and b label the Cartesian components. Our two-particle density is

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2, \qquad (5)$$

which, if approximated by an antisymmetric product of single-particle orbitals $\psi_i(\mathbf{r})$ and $\psi_j(\mathbf{r})$, may be expressed as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2) - \psi_i(\mathbf{r}_2)\psi_j(\mathbf{r}_1)]. \qquad (6)$$

Since f_{ab} is identical under particle exchange, we may write

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$$\rho(\mathbf{r}_1,\mathbf{r}_2) = \psi_i(\mathbf{r}_1)\psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_2)\psi_j^*(\mathbf{r}_2) - \psi_i(\mathbf{r}_1)\psi_i^*(\mathbf{r}_2)\psi_j(\mathbf{r}_2)\psi_j^*(\mathbf{r}_1) \tag{7}$$

and

$$D_{ab}(i,j) = \frac{1}{2}(J_{ij}^{ab} - K_{ij}^{ab}), \tag{8}$$

where

$$J_{ij}^{ab} = \int\int \psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)f_{ab}(\mathbf{r}_1-\mathbf{r}_2)\psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{9}$$

and

$$K_{ij}^{ab} = \int\int \psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)f_{ab}(\mathbf{r}_1-\mathbf{r}_2)\psi_i^*(\mathbf{r}_2)\psi_j^*(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_2. \tag{10}$$

Numerical evaluation of these integrals is very demanding, both in terms of computational cost and stability—some care needs to be taken with the integrand when $\mathbf{r}_1=\mathbf{r}_2$. The usual approach in a quantum chemistry code would be to use an underlying expansion of the states $\{\psi_i\}$ in terms of atom-centered functions, which would convert (9) and (10) into expressions that involve the products of four such functions centered on different sites. These integrals are related to derivatives of the usual four center integrals used to evaluate the Hartree and exchange energies. We have not pursued this approach, however, as it is much less efficient when implemented for a periodic system. Instead we expand $\rho(\mathbf{r}_1,\mathbf{r}_2)$ in plane waves,

$$\rho(\mathbf{r}_1,\mathbf{r}_2) = \sum_{\mathbf{G}_1\mathbf{G}_2} \rho(\mathbf{G}_1,\mathbf{G}_2)e^{i\mathbf{G}_1\cdot\mathbf{r}_1}e^{i\mathbf{G}_2\cdot\mathbf{r}_2}, \tag{11}$$

which yields [with the change of variables $\mathbf{r}_1=\frac{1}{2}(\mathbf{R}+\mathbf{r})$ and $\mathbf{r}_2=\frac{1}{2}(\mathbf{R}-\mathbf{r})$]

$$I_{ab} = \frac{1}{8}\sum_{\mathbf{G}_1\mathbf{G}_2}\rho(\mathbf{G}_1,\mathbf{G}_2)\int\int e^{i[\mathbf{r}\cdot(\mathbf{G}_1-\mathbf{G}_2)]/2} \times e^{i[\mathbf{R}\cdot(\mathbf{G}_1+\mathbf{G}_2)]/2}f_{ab}(\mathbf{r})d\mathbf{r}\,d\mathbf{R}. \tag{12}$$

Integrating over $\mathbf{R}$ gives $8\Omega\delta_{\mathbf{G}_1,-\mathbf{G}_2}$, so $\mathbf{G}_1=-\mathbf{G}_2$, and Eq. (12) simplifies to

$$I_{ab} = \Omega\sum_{\mathbf{G}}\rho(\mathbf{G},-\mathbf{G})\int e^{i\mathbf{G}\cdot\mathbf{r}}f_{ab}(\mathbf{r})d\mathbf{r}, \tag{13}$$

where Ω is the volume of the unit cell. This integral may be evaluated starting from the standard result

$$\int e^{i\mathbf{G}\cdot\mathbf{r}}\frac{1}{|\mathbf{r}-\mathbf{C}|}d\mathbf{r} = \frac{4\pi}{G^2}e^{i\mathbf{G}\cdot\mathbf{C}}. \tag{14}$$

Differentiating this twice gives

$$-\frac{\partial^2}{\partial C_a C_b}\int\frac{e^{i\mathbf{G}\cdot\mathbf{r}}}{|\mathbf{r}-\mathbf{C}|}d\mathbf{r} = \frac{4\pi G_a G_b}{G^2}e^{i\mathbf{G}\cdot\mathbf{C}}. \tag{15}$$

We now note that

$$\frac{\partial^2}{\partial C_a C_b}\left(\frac{1}{|\mathbf{r}-\mathbf{C}|}\right) = \frac{3r'_a r'_b}{|\mathbf{r}'|^5} - \frac{\delta_{ab}}{|\mathbf{r}'|^3} - \frac{4\pi\delta_{ab}}{3}\delta(\mathbf{r}'), \tag{16}$$

where $\mathbf{r}'=\mathbf{r}-\mathbf{C}$. Inserting this into Eq. (15) gives

$$\int e^{i\mathbf{G}\cdot\mathbf{r}}\left(\frac{(r')^2\delta_{ab}-3r'_a r'_b}{(r')^5}\right)d\mathbf{r} = \frac{4\pi G_a G_b}{G^2}e^{i\mathbf{G}\cdot\mathbf{C}} + \frac{4\pi}{3}\delta_{ab}.$$

We finally set $\mathbf{C}=\mathbf{0}$ to obtain

$$I_{ab} = 4\pi\Omega\sum_{\mathbf{G}}\rho(\mathbf{G},-\mathbf{G})\left(\frac{G_a G_b}{G^2} - \frac{\delta_{ab}}{3}\right) = J_{ij}^{ab} - K_{ij}^{ab}. \tag{17}$$

B. Many-particle system

Many calculations of the D tensor assume the relevant wave function to be satisfactorily described by the unpaired electrons occupying the highest spin-up Kohn-Sham orbitals[3,4] and in some cases such calculations produce good results. This is particularly the case when the unpaired Kohn-Sham states are well separated in energy from other occupied states, with the result that spin polarization of the valence band is small. We have found[3–5] that many defect centers in diamond are well treated in this way. However, as was noted in Ref. 5, some systems require that valence states are also included. We now generalize the above formalism to calculations involving more than two states. The full many-particle D tensor is given by[14]

$$D_{ab} = \langle\Psi|\hat{D}|\Psi\rangle = \frac{1}{S(2S-1)}\langle\Psi|\sum_{i<j}f_{ab}(\mathbf{r}_i,\mathbf{r}_j)(2\hat{s}_{i_z}\hat{s}_{j_z} - \hat{s}_{i_y}\hat{s}_{j_y} - \hat{s}_{i_x}\hat{s}_{j_x})|\Psi\rangle$$

$$= \frac{1}{S(2S-1)}\Big(\frac{1}{2}\langle\Psi|\sum_{i<j}f_{ab}(\mathbf{r}_i,\mathbf{r}_j)\hat{\sigma}_{i_z}\hat{\sigma}_{j_z}|\Psi\rangle - \frac{1}{4}\langle\Psi|\sum_{i<j}f_{ab}(\mathbf{r}_i,\mathbf{r}_j)\hat{\sigma}_{i_x}\hat{\sigma}_{j_x} + \sum_{i<j}f_{ab}(\mathbf{r}_i,\mathbf{r}_j)\hat{\sigma}_{i_y}\hat{\sigma}_{j_y}|\Psi\rangle\Big). \tag{18}$$

If there is significant spin polarization of the valence states, they should be included in the calculation. Although this brings the possibility of spin contamination it has been noted in the past[17] that Kohn-Sham states suffer less from this phenomenon than, for example, Hartree-Fock orbitals. Allowing Ψ to be constructed from an unrestricted Slater determinant of single-particle orbitals, with p spin-up (α) and q spin-down (β), we may proceed to evaluate the total D tensor in a manner very similar to the standard derivation of the Hartree-Fock equations—the only difference being that $\hat{D}$ is a spin-dependent operator. The effect of the Pauli operators on spin functions is as follows:

$$\hat{\sigma}_x|\alpha\rangle = |\beta\rangle, \quad \hat{\sigma}_x|\beta\rangle = |\alpha\rangle, \tag{19}$$

$$\hat{\sigma}_y|\alpha\rangle = i|\beta\rangle, \quad \hat{\sigma}_y|\beta\rangle = -i|\alpha\rangle, \tag{20}$$

$$\hat{\sigma}_z|\alpha\rangle = |\alpha\rangle, \quad \hat{\sigma}_z|\beta\rangle = -|\beta\rangle. \tag{21}$$

The term containing $\hat{\sigma}_z$ in Eq. (18) differs from the spin-independent expression only by a change of sign in the J_{ij}^{ab} term if spins are antiparallel, giving

$$\frac{1}{2}\left(\sum_{i<j}^{p+q} J_{ij}^{ab}\chi_{ij} - \sum_{i<j}^{p} K_{ij}^{ab,\alpha} - \sum_{i<j}^{q} K_{ij}^{ab,\beta}\right), \tag{22}$$

where $\chi_{ij}=+1$ if spins are parallel and $\chi_{ij}=-1$ if spins are antiparallel. The superscript α or β denotes that only orbitals with parallel spins are included. The terms containing $\hat{\sigma}_x$ and $\hat{\sigma}_y$ in Eq. (18) both flip the spin of the function they operate on and so can be treated in a similar manner. Due to the effect of $\hat{\sigma}_x$ and $\hat{\sigma}_y$, only exchange terms with antiparallel spins will integrate to a finite result. For spin-independent operators these terms vanish upon integration over spin space, however, the spin *flipping* of $\hat{\sigma}_x$ and $\hat{\sigma}_y$ results in exchange terms with parallel spin functions vanishing instead. Putting these terms together, with an extension of the notation, we have

$$D_{ab} = \frac{1}{2S(2S-1)}\left(\sum_{i<j}^{p+q} J_{ij}^{ab}\chi_{ij} - \sum_{i<j}^{p} K_{ij}^{ab,\alpha} - \sum_{i<j}^{q} K_{ij}^{ab,\beta} - \sum_{i<j}^{p+q} K_{ij}^{ab,\alpha\beta}\right), \tag{23}$$

where the superscript $\alpha\beta$ denotes only the inclusion of states with antiparallel spins. As a direct extension of the expression given for the two-particle system (8) the general result can be written compactly as

$$D_{ab} = \sum_{i<j} D_{ab}(i,j)\chi_{ij}. \tag{24}$$

Finally, $\mathbf{D}$ is diagonalized to obtain the eigenvalues and principal directions.

C. Brillouin zone sampling

Finally, we turn to the issue of $\mathbf{k}$-point sampling as it is often necessary to sample the Brillouin zone at several points to adequately describe the charge density or the Kohn-Sham orbitals. This can be done, using the above formalism, simply by evaluating $\rho(\mathbf{r}_1,\mathbf{r}_2)$ as a sum over $\mathbf{k}$ points,

$$\rho(\mathbf{r}_1,\mathbf{r}_2) = \sum_{\mathbf{k}} \omega_{\mathbf{k}}\rho_{\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2), \tag{25}$$

using, for example, Brillouin zone sampling as presented in Ref. 18.

III. COMPUTATIONAL DETAILS

Equation (17) is very straightforward to evaluate computationally and is a significant simplification of the original six-dimensional integral.

The quantity $\rho(\mathbf{G},-\mathbf{G})$ is evaluated in the following way:

(1) Evaluate the functions $\psi_i(\mathbf{r})$ and $\psi_j(\mathbf{r})$ on a real space grid.

(2) On this grid tabulate the functions $f_1(\mathbf{r})=|\psi_i(\mathbf{r})|^2$, $f_2(\mathbf{r})=|\psi_j(\mathbf{r})|^2$, and $f_3(\mathbf{r})=\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})$, operating point by point.

(3) Fourier transform these three functions to get $f_1(\mathbf{G})$, $f_2(\mathbf{G})$, and $f_3(\mathbf{G})$.

(4) $\rho(\mathbf{G},-\mathbf{G})=f_1(\mathbf{G})f_2(-\mathbf{G})-|f_3(\mathbf{G})|^2$.

The evaluation of ρ using this and the subsequent calculation of the D tensor using (17) is extremely rapid on modern computers and scales as $O(N\log N)$ if the number of states included is independent of system size. Our present implementation scales cubically with system size when all valence states are included; however, the sum in Eq. (24) can be parallelized trivially.

Code to evaluate the above was written using both shared memory communication and the message passing interface. Arbitrary Fourier transform grids may be chosen to provide sufficient memory and almost perfect scaling on massively parallel supercomputers.

Results presented using the above method[3–7] have used the pseudopotential approximation and have neglected the spin-orbit contribution to the zero-field tensor. However, the dominant contribution to the D tensor, due to the $|\mathbf{r}_1-\mathbf{r}_2|^{-5}$ factor, comes from the valence region, so core corrections (although strictly necessary) may be omitted. The inclusion of spin-orbit contributions, however, will be more important when considering heavy elements.

IV. CONCLUSION

The formalism for the efficient and stable evaluation of the zero-field splitting tensor from periodic Kohn-Sham density functional calculations has been presented. This method has been used in several studies of defect centers in diamond and silicon. The formalism presented above can be easily implemented in any periodic DFT electronic-structure code, and we hope this will increase the theoretical calculation of zero-field splitting tensors for high-spin defect centers.

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