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The Second-Order Energy Contribution from the Spin–Orbit Interaction Operator to the Potential Energy Curve of Cr₂

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Abstract

The second-order Rayleigh–Schrödinger energy correction to the Born–Oppenheimer potential energy due to the spin–orbit interaction can be expressed as a linear response function evaluated at zero frequency. We have calculated this energy contribution to the Cr₂ singlet ground state $X^1\Sigma_g^+$ potential energy function for a multiconfiguration self-consistent field (MCSCF) wave function. The calculations show that the effect of spin–orbit interaction is small and of the same magnitude for the whole potential energy curve.

The Cr₂ molecule with its hexuple bond is a cause célèbre in electronic structure calculations. No method so far has been able to give a satisfactory description of its binding [1, 2]. Much of the problems encountered in these calculations are related to the hexuple bond of the Cr₂ molecule with the entailed problem of describing the electron correlation. Moreover, the presence of several close-lying excited states and the unusually shallow potential energy curve of the ground state make it plausible that finer effects such as relativistic and nonadiabatic couplings may be important for the binding energy and the bond length. For Cr₂ even small energy contributions may be important if they show large variations with geometry. Relativistic effects in general have been claimed to be important [2]. Because of possible coupling to close-lying excited triplet states one such candidate is the spin–orbit interaction. In this communication we investigate the importance of the spin–orbit operator by carrying out a second-order Rayleigh–Schrödinger energy calculation with the spin–orbit operator as a perturbation. It is the first application of the multiconfiguration spin–orbit response method recently presented in Ref. 3.

The spin–orbit operator is

$$H_{\text{SO}} = \frac{\alpha^2}{2} \left[\sum_{iA} Z_A \frac{\mathbf{l}_{iA} \cdot \mathbf{s}_i}{r_{iA}^3} - \sum_{ij} \frac{\mathbf{l}_{ij} \cdot (\mathbf{s}_i + 2\mathbf{s}_j)}{r_{ij}^3} \right], \quad (1)$$

where i, j refer to electrons and A to nuclei. \mathbf{r}_{ij} is the position of particle i relative to particle j and $\mathbf{l}_{ij} = \mathbf{r}_{ij} \times \mathbf{p}_i$ is the orbital angular momentum of particle i with respect to the position of particle j . Z_A is the charge of nucleus A and α the fine-structure constant.

The second-order energy contribution from the spin-orbit operator is

$$\epsilon_0^{(2)} = \sum_n \frac{\langle 0 | H_{\text{SO}} | n \rangle \langle n | H_{\text{SO}} | 0 \rangle}{E_0 - E_n} \quad (2)$$

where $|0\rangle$ is the reference state with total energy E_0 and $|n\rangle$ an excited state with total energy E_n . The spin-orbit operator contains both one- and two-electron terms and the second-order energy contribution may therefore show large variations with respect to the bond length.

In this paper we calculate the second-order energy contribution, Eq. (2), to the potential energy curve of Cr_2 . The simplest reasonable description of the Cr_2 potential energy curve is obtained in a complete active space (CAS) calculation keeping the $4s$ and $3d$ orbitals active resulting in a 12 electrons in 12 orbitals calculation. This calculation would allow for a correct dissociation of the hexuple bond [4]. Using the $(14s11p6d)/[8s4p2d]$ basis set given in Ref. 5, we have determined the second-order energy contribution in Eq. (2) by calculating the linear response function for the 12-in-12 CAS reference wave function at zero frequency [6]:

$$\langle\langle H_{\text{SO}}; H_{\text{SO}} \rangle\rangle_{\omega=0} = V^{(1)}(E^{(2)})^{-1}V^{(1)} \quad (3)$$

where

$$E^{(2)} = \begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \quad (4)$$

and the matrices A and B are given by

$$A = \begin{pmatrix} \langle 0 | [q_i, [H_0, q_j^\dagger]] | 0 \rangle & \langle 0 | [[q_i, H_0], R_j^\dagger] | 0 \rangle \\ \langle 0 | [R_i, [H_0, q_j^\dagger]] | 0 \rangle & \langle 0 | [[R_i, H_0], R_j^\dagger] | 0 \rangle \end{pmatrix} \quad (5)$$

$$B = \begin{pmatrix} \langle 0 | [q_i, [H_0, q_j]] | 0 \rangle & \langle 0 | [[q_i, H_0], R_j] | 0 \rangle \\ \langle 0 | [R_i, [H_0, q_j]] | 0 \rangle & \langle 0 | [[R_i, H_0], R_j] | 0 \rangle \end{pmatrix} \quad (6)$$

q_i^\dagger refer to a nonredundant orbital excitation operator and R_j^\dagger to a state transfer operator $|j\rangle\langle 0|$ connecting the MCSCF reference wave function $|0\rangle$ and the state $|j\rangle$ belonging to the orthogonal complement set to $|0\rangle$. The vector $V^{(1)}$ is defined as

$$V^{(1)} = \begin{bmatrix} \langle 0 | [q, H_{\text{SO}}] | 0 \rangle \\ \langle j | H_{\text{SO}} | 0 \rangle \\ \langle 0 | [q^\dagger, H_{\text{SO}}] | 0 \rangle \\ -\langle 0 | H_{\text{SO}} | j \rangle \end{bmatrix} \quad (7)$$

The linear response function in Eq. (3) gives twice the second-order energy contribution in Eq. (2). To determine Eq. (3) we need to solve the linear set of equations

$$E^{(2)}X = V^{(1)} \quad (8)$$

This is done in the configuration state function basis using the iterative technique described in Ref. 7. The linear transformations required in the iterative

TABLE I. Second-order energy contribution from the spin-orbit operator to the Born-Oppenheimer potential energy curve of Cr₂.

Internuclear distance a.u.	Total energy a.u.	Second-order energy contribution a.u.		
		x, y component	z component	Total
2.0	-2084.753725	-0.006192	-0.006152	-0.018537
3.0	-2086.382671	-0.006159	-0.006142	-0.018461
4.0	-2086.442957	-0.006148	-0.006146	-0.018441
5.0	-2086.469319	-0.006145	-0.006145	-0.018436

^aThe z axis is the internuclear axis.

algorithm

$$\sigma = E^{(2)}b \quad (9)$$

are carried out as described in Ref. 8.

The calculated energy corrections are given in Table I. The potential energy curve we calculate is slightly above but parallel to the one obtained by Walch et al. [4]. The results show that the spin-orbit contribution to the potential energy is small and that the geometry dependence is negligible both for the one- and the two-electron parts. Even though the CAS wave function does not give a quantitatively correct description of the binding of Cr₂, it contains the major elements of the exact wave function. We may therefore conclude that the contribution from the spin-orbit operator due to close-lying triplet states can be neglected for the binding energy of Cr₂. We have thus eliminated yet another cause for the problems in calculations of the binding of Cr₂.

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