

g-Matrix Based on Configuration Interaction and Stone's Perturbation Theory¹

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Stone's formula, which has usually been applied to the calculation of the *g*-matrix, is based on a single-configuration treatment. Here a limited configuration interaction is included to obtain the expressions of the principal *g* values for an orbitally nondegenerate molecule with spin $S = \frac{1}{2}$. © 1999 Academic Press

Key Words: *g*-matrix; Stone's formula; configuration interaction; doublet states; orbitally nondegenerate state.

INTRODUCTION

Stone derived a gauge-invariant formula for the principal *g* values of an orbitally nondegenerate molecule based on single-configuration theory (*I*). Up to now, the formula has generally been applied to calculation of the *g*-matrix (2–10). It is well known, however, that the single-configuration molecular orbital treatment is not reliable for open-shell molecules or the excited states that must be considered in calculating EPR parameters. Configuration interaction has been proved to be an effective method for coping with excited states or ground states with open shells (11–19). In order to use CI treatment in calculation of the *g*-matrix, a new formula must be established based on multiple-configuration wave functions. From Stone's gauge-invariant spin Hamiltonian, here we deduce the multiple-configuration expressions for the principal *g* values of a molecule in an orbitally nondegenerate state with $S = \frac{1}{2}$.

STONE'S PERTURBATION THEORY

According to Stone's perturbation theory (*I*), the gauge-invariant spin Hamiltonian is given by

$$\mathcal{H} = E_0 + 2\beta\mathbf{H} \cdot \mathbf{S} + P_0\mathcal{H}_2P_0 - \sum_{n \neq 0} \frac{P_0\mathcal{H}_1P_n\mathcal{H}_1P_0}{E_n - E_0}. \quad [1]$$

The meanings of all symbols used in this paper are taken from Stone (*I*) except when specially indicated. The second-order quantities in the magnetic field (i.e., quantities in \mathbf{H}^2)

make no contribution to the *g*-matrix;² therefore, $P_0\mathcal{H}_2P_0$ is left as

$$\begin{aligned} & \frac{e}{2\hbar c} \sum_{m,m'} |0, m\rangle \langle 0, m| \sum_{i,k} (\mathbf{d}_i \cdot \mathbf{r}_{ki} \delta^{\alpha\beta} - r_{ki}^{\alpha} d_i^{\beta}) \\ & \times \xi_k(r_{ki}) H^{\alpha} S_i^{\beta} |0, m'\rangle \langle 0, m'|, \end{aligned} \quad [2]$$

where the summation convention is assumed for all Greek superscripts. For the last term of Eq. [1], we ignore the quantities in \mathbf{H}^2 for the same reason as above and the second-order spin-orbit coupling terms, which cannot separate the levels of a spin doublet,² and obtain

$$\begin{aligned} P_0\mathcal{H}_1P_n\mathcal{H}_1P_0 &= 2\beta \sum_{m,m'} |0, m\rangle \langle 0, m| \sum_i \mathbf{l}'_i \cdot \mathbf{H} |n, m\rangle \\ &\times \langle n, m'| \sum_{i,k} \xi_k(r_{ki}) \mathbf{l}_{ki} \cdot \mathbf{S}_i |0, m'\rangle \langle 0, m'|. \end{aligned} \quad [3]$$

As the coordinate axes can be chosen to make $g^{\alpha\beta}$ diagonal, only the principal values of g^{xx} , g^{yy} , and g^{zz} need calculating. For simplicity, we only give the detailed process for calculating g^{zz} . The expressions for g^{xx} and g^{yy} can be obtained in the same way.

When only g^{zz} is considered, the terms of interest in Eq. [1] can be collected as

$$\beta g^{zz} H^z S^z = 2\beta H^z S^z + P_0\mathcal{H}_2P_0 - \sum_{n \neq 0} \frac{P_0\mathcal{H}_1P_n\mathcal{H}_1P_0}{E_n - E_0}, \quad [4]$$

where

$$\begin{aligned} P_0\mathcal{H}_2P_0 &= \frac{eH^z}{2\hbar c} \sum_{m,m'} |0, m\rangle \langle 0, m| \sum_{k,i} (\mathbf{d}_i \cdot \mathbf{r}_{ki} - r_{ki}^z d_i^z) \\ &\times \xi_k(r_{ki}) S_i^z |0, m'\rangle \langle 0, m'| \end{aligned} \quad [5]$$

$$\begin{aligned} P_0\mathcal{H}_1P_n\mathcal{H}_1P_0 &= 2\beta H^z \sum_{m,m'} |0, m\rangle \langle 0, m| \sum_i l_i^z |n, m\rangle \\ &\times \langle n, m'| \sum_{i,k} \xi_k(r_{ki}) l_{ki}^z S_i^z |0, m'\rangle \langle 0, m'|. \end{aligned} \quad [6]$$

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² See Eqs. [54]–[60] in Section 4 of Stone's paper (*I*).

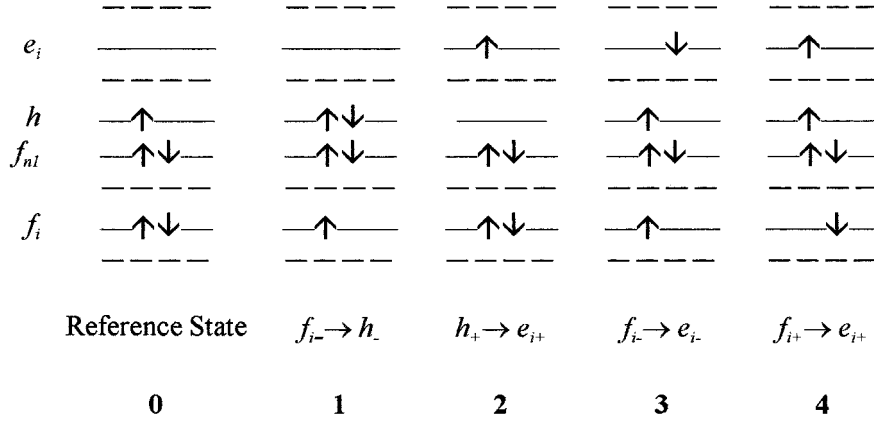


FIG. 1. Single excitations for the doublet states of systems with $S = \frac{1}{2}$, where e , f , and h correspond to empty, filled, and half-filled MOs (spin-orbitals) determined in the reference state calculation.

Although the expression [4] is gauge-invariant, $P_0\mathcal{H}_2P_0$ and $P_0\mathcal{H}_1P_n\mathcal{H}_1P_0$ are not gauge-invariant by themselves, since \mathbf{d} is the position vector of the electron relative to some arbitrary origin, and \mathbf{l} is the angular momentum about the origin of \mathbf{d} . In order to get a complete gauge-invariant expression, we must rewrite Eqs. [5] and [6].

Because of spin symmetry, only the excited states with $S_z = \frac{1}{2}$ and $S^2 = 1$ can be mixed into the ground state; therefore, only the terms with $m = m' = \frac{1}{2}$ are left in the first sum of Eq. [6]. Thus

$$P_0\mathcal{H}_1P_n\mathcal{H}_1P_0 = 2\beta H^z \langle 0 | \sum_i l_i^z | n \rangle \cdot \langle n | \sum_{i,k} \xi_k(r_{ki}) l_{ki}^z S_i^z | 0 \rangle. \quad [7]$$

If the state wavefunctions of $\langle n |$ ($n = 0, 1, 2 \dots$) were expressed by single configurations, Eqs. [1]–[7] would lead to Stone's formula (I). When CI treatment is involved, the wavefunctions are represented by multiconfigurations as

$$\langle n | = \sum_I A_n I \Phi_I, \quad [8]$$

where each configuration Φ is approximated as a Slater determinant. Substituting [8] into [7], we obtain

$$P_0\mathcal{H}_1P_n\mathcal{H}_1P_0 = 2\beta H^z \sum_{I,J,K,L} A_0 I A_n J A_n K A_0 L \times \sum_k \langle \Phi_I | F_1 | \Phi_J \rangle \langle \Phi_K | F_2 | \Phi_L \rangle, \quad [9]$$

where

$$F_1 = \sum_i l_i^z \quad [10]$$

$$F_2 = \sum_i \xi_k(r_{ki}) l_{ki}^z S_i^z. \quad [11]$$

Since the g -matrix of an orbitally nondegenerate molecule with $S = \frac{1}{2}$ is dominantly contributed by the doublet ground state and a few low-lying excited doublet states, it is usually considered sufficient to include only the single excitation in LCI (limited configuration interaction), and the number of configurations to be treated in the CI matrix is limited by a preset energy criterion (9–10 eV) (15). The ground reference state is usually calculated by the Hartree–Fock method, and the excited states are generated by LCI among configurations formed by single-electron excitation from occupied MOs into unoccupied or virtual orbitals determined in the reference state calculation. There are five types of relevant doublet states shown in Fig. 1.

By comparison of the initial configuration ($\langle \Phi_J |$ or $\langle \Phi_L |$) and the end configuration ($\langle \Phi_I |$, $\langle \Phi_K |$) in $\langle \Phi_I | F_1 | \Phi_J \rangle$ and $\langle \Phi_K | F_2 | \Phi_L \rangle$ we classify the excitation-matrix elements into three cases based on Fig. 1:

- (a) no excitation (the initial configuration is the same as the end);
- (b) double excitation (the initial and the end Φ are related by double excitation);
- (c) single excitation (the initial and the end Φ are related by single excitation).

First, let us calculate $\langle \Phi_I | F_1 | \Phi_J \rangle$ according to the three cases above.

(a') *No Excitation*

According to the symmetry principle, only the orbitally nondegenerate excited configurations can be included in the ground state; thus the total angular momentum of the molecule averaged over the ground state is zero, that is to say, the diagonal elements of the F_1 matrix are zero.

(b') *Double Excitation*

The F_1 matrix element can be expressed as the summation over one-electron operator matrix elements,

$$\langle \Phi_I | \sum_i l_i^z | \Phi_J \rangle = \sum_i \langle \Phi_I | l_i^z | \Phi_J \rangle. \quad [12]$$

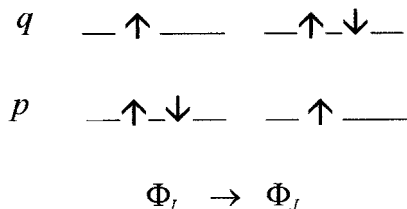


FIG. 2. Single excitation for $p_- \rightarrow q_-$ (Φ_i and Φ_j differ only in orbitals $\langle p|$ and $\langle q|$).

Since a single-electron operator cannot excite two electrons at one time, every term on the right-hand side of [12] is zero; thus

$$\langle \Phi_i | F_1 | \Phi_j \rangle = 0.$$

(c') Single Excitation

Figure 2 indicates a single excitation by which a β electron ($m_s = -\frac{1}{2}$) is transited to q from p , which is symbolized as $p_- \rightarrow q_-$. With the use of the determinantal symbol $\det |\cdot \cdot \cdot|$,³ we write $\langle \Phi_i | F_1 | \Phi_j \rangle$ as

$$K^2 \cdot \langle \det |\cdot \cdot \cdot p_+ q_+ p_-| | F_1 | \det |\cdot \cdot \cdot p_+ q_+ q_-| \rangle, \quad [13]$$

where

$$K = \frac{1}{\sqrt{t!}},$$

and t is the number of total electrons in the molecule. Expanding the determinant, we get $(t!)^2$, adding terms of the type (each way of ranking gives a similar term)

$$\begin{aligned}
 & K^2 \langle \cdot \cdot \cdot p_+(t-2)q_+(t-1) \\
 & \times p_-(t) | F_1 | \cdot \cdot \cdot p_+(t-2)q_+(t-1)q_-(t) \rangle. \quad [14]
 \end{aligned}$$

Writing [14] as the sum of one-electron operator matrix elements, we have as the t th electron's matrix element

$$\begin{aligned}
 & K^2 \langle \cdot \cdot \cdot p_+(t-2)q_+(t-1)p_-(t) \\
 & \times | l' z \rangle | \cdot \cdot \cdot p_+(t-2)q_+(t-1)q_-(t) \rangle. \quad [15]
 \end{aligned}$$

Therefore, after expanding the determinantal matrix element of [13], we obtain $t!t!$ added terms of one-electron matrix elements of the type [15], of which the nonzero terms are those satisfying the following two conditions:

Condition A. The ranks of the electrons are equal for both sides of the operator.

Condition B. The one-electron operator must act on the excited electron.

³ As a regulation for the symbol $\det |\cdot \cdot \cdot|$, the MOs are arranged in order so that the MOs with no electron excitation are ranked in the front and the same order is followed for both sides of the operator; the MOs in which the electrons are excited in or out are ranked at the end.

If the orthonormality constraint $\langle i | j \rangle = \delta_{ij}$ is assumed for all MOs, the remaining terms of the type [15] can be written

$$K^2 \langle p_-(i) | l' z | q_-(i) \rangle, \quad [16]$$

where i represents the excited electron, which is not identical for different terms. Because of the indistinguishability of all electrons, [16] is replaced with

$$K^2 \langle p_- | l' z | q_- \rangle. \quad [17]$$

Since the angular momentum operator does not act on the spin functions, [17] is equal to

$$K^2 \langle p | l' z | q \rangle. \quad [18]$$

As a result, all the remaining terms of [15] have the same value. There are $t!$ ways to rank the electrons, so there are $t!$ terms of the type [14] satisfying Condition A, of which only one term of the type [15] satisfies Condition B. Thus $t!$ terms of the type [18] are left in $\langle \Phi_i | F_1 | \Phi_j \rangle$. Since

$$\begin{aligned}
 & K^2 = \frac{1}{t!}, \\
 & \langle \Phi_i | F_1 | \Phi_j \rangle = \langle p | l' z | q \rangle.
 \end{aligned}$$

Extending the excitation shown in Fig. 2 to the general cases $i_{\pm} \rightarrow j_{\pm}$, we have

$$\langle \Phi_i | F_1 | \Phi_j \rangle = \langle i | l' z | j \rangle.$$

All possible matrix elements of $\langle \Phi_i | F_1 | \Phi_j \rangle$ constructed from the five types of configurations given in Fig. 1 are listed in Table 1.

Next we must calculate $\langle \Phi_k | F_2 | \Phi_l \rangle$. In the same way, it can be calculated according to cases (a), (b), and (c).

(a'') No Excitation

According to Fig. 1, there are two kinds of no-excitation matrix elements categorized by the number of the half-filled MOs, which are shown in Fig. 3.

Let us deal with Fig. 3a first. Write $\langle \Phi_k | F_2 | \Phi_l \rangle$ in the determinantal form,

$$\begin{aligned}
 & K^2 \cdot \langle \det | f_1 + f_1 - \cdot \cdot \cdot f_n + f_n - h_1 + h_2 + h_3 - | \\
 & \times | F_2 | \det | f_1 + f_1 - \cdot \cdot \cdot f_n + f_n - h_1 + h_2 + h_3 - | \rangle. \quad [19]
 \end{aligned}$$

Expand [19] to the sum of $t!$ terms of the following type:

TABLE 1
The Calculations of $\langle \Phi_I | F_1 | \Phi_J \rangle^a$

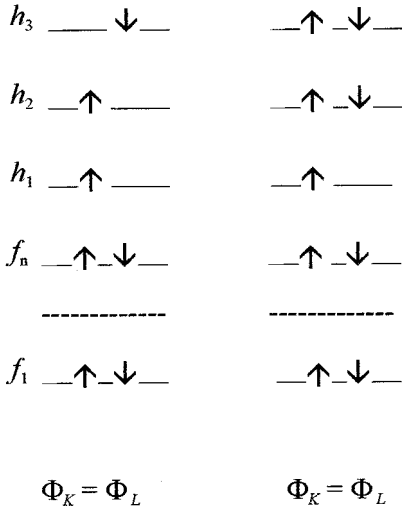
Configuration type		Excitations for single configuration		Electron excitations for $\langle \Phi_I F_1 \Phi_J \rangle$	$\langle \Phi_I F_1 \Phi_J \rangle$ = $\langle p l' z q \rangle$	Category
$I (\Phi_I)$	$J (\Phi_J)$	Φ_I	Φ_J			
0	0	No excitation	No excitation	No excitation	0	a
0	1	No excitation	$f_{i-} \rightarrow h_-$	$f_{i-} \rightarrow h_-$	$\langle f_i l' z h \rangle$	c
0	2	No excitation	$h_+ \rightarrow e_{l+}$	$h_+ \rightarrow e_{l+}$	$\langle h l' z e_i \rangle$	c
0	3	No excitation	$f_{i-} \rightarrow e_{l-}$	$f_{i-} \rightarrow e_{l-}$	$\langle f_i l' z e_i \rangle$	c
0	4	No excitation	$f_{i+} \rightarrow e_{l+}$	$f_{i+} \rightarrow e_{l+}$	$\langle f_i l' z e_i \rangle$	c
1	1	$f_{i-} \rightarrow h_-$	$f_{j-} \rightarrow h_-$	$f_{j-} \rightarrow f_{i-}$	$\langle f_j l' z f_i \rangle$	c
1	2	$f_{i-} \rightarrow h_-$	$h_+ \rightarrow e_{l+}$	2e	0	b
1	3	$f_{i-} \rightarrow h_-$	$f_{j-} \rightarrow e_{l-}$	$i = j: h_- \rightarrow e_{l-}$ $i \neq j: 2e$	$\langle h l' z e_i \rangle$ 0	c b
1	4	$f_{i-} \rightarrow h_-$	$f_{j+} \rightarrow e_{l+}$	2e	0	b
2	2	$h_+ \rightarrow e_{l+}$	$h_+ \rightarrow e_{k+}$	$e_{l+} \rightarrow e_{k+}$	$\langle e_l l' z e_k \rangle$	c
2	3	$h_+ \rightarrow e_{l+}$	$f_{i-} \rightarrow e_{k-}$	2e	0	b
2	4	$h_+ \rightarrow e_{l+}$	$f_{i+} \rightarrow e_{k+}$	$l = k: f_{i+} \rightarrow h_+$ $l \neq k: 2e$	$\langle f_i l' z h \rangle$ 0	c b
3	3	$f_{i-} \rightarrow e_{l-}$	$f_{j-} \rightarrow e_{k-}$	$i = j: e_{l-} \rightarrow e_{k-}$ $l = k: f_{j-} \rightarrow f_{i-}$ $l \neq j \text{ and } l \neq k: 2e$	$\langle e_l l' z e_k \rangle$ $\langle f_j l' z f_i \rangle$ 0	c c b
3	4	$f_{i-} \rightarrow e_{l-}$	$f_{j+} \rightarrow e_{k+}$	2e	0	b
4	4	$f_{i+} \rightarrow e_{l+}$	$f_{j+} \rightarrow e_{k+}$	$l = j: e_{l+} \rightarrow e_{k+}$ $l = k: f_{j+} \rightarrow f_{i+}$ $l \neq j \text{ and } l \neq k: 2e$	$\langle e_l l' z e_k \rangle$ $\langle f_j l' z f_i \rangle$ 0	c c b

^a 2e indicates the excitations of more than two electrons.

$$\begin{aligned}
& K^2 \langle f_{1+}(1) f_{1-}(2) \dots h_{1+}(t-3)(t-2) h_{2+}(t-1) h_{3-}(t) \\
& \times |F_2| f_{1+}(1) f_{1-}(2) \dots h_{1+}(t-3)(t-2) \\
& \times h_{2+}(t-1) h_{3-}(t) \rangle. \quad [20]
\end{aligned}$$

$$\begin{aligned}
& K^2 \langle f_{1+}(1) f_{1-}(2) \dots h_{1+}(t-3)(t-2) h_{2+}(t-1) h_{3-}(t) \\
& \times |\xi_k(r_{ki}) l_{ki}^z S_i^z | f_{1+}(1) f_{1-}(2) \dots h_{1+}(t-3) \\
& \times (t-2) h_{2+}(t-1) h_{3-}(t) \rangle. \quad [21]
\end{aligned}$$

Write [20] as the sum of one-electron operator matrix elements, and we get the i th electron's element,



(a)

(b)

Expression [21] is nonzero only when the electrons are ranked in the same order on both sides of the operator (Condition **A**). With no electron excitation, Condition **B** does not work here. Thus the sum over electrons can be replaced by a sum over orbitals (see Footnote 2), and [20] is equal to

$$K^2 \sum_i \langle i_{\pm} | \xi_k(r_k) l_k^z S_i^z | i_{\pm} \rangle,$$

where $|i_{\pm}\rangle$ indicates a certain MO (spin-orbital function with $m_s = \pm \frac{1}{2}$). Separate the spin and orbital variables, and the expression above is equal to

$$K^2 \sum_i \pm S^z \langle i | \xi_k(r_k) l_k^z | i \rangle. \quad [22]$$

The filled orbitals do not contribute, since the spin parts cancel, and we are left with

$$\begin{aligned}
\langle \Phi_K | F_2 | \Phi_L \rangle &= \langle h_1 | \xi_k(r_k) l_k^z | h_1 \rangle + \langle h_2 | \xi_k(r_k) l_k^z | h_2 \rangle \\
&\quad - \langle h_3 | \xi_k(r_k) l_k^z | h_3 \rangle. \quad [23]
\end{aligned}$$

FIG. 3. Two kinds of no-excitation matrix element.

TABLE 2
The Calculations of $\langle \Phi_K | F_2 | \Phi_L \rangle$

Configuration type		Excitations for single configurations		Excitations of electrons for $\langle \Phi_K F_2 \Phi_L \rangle$	$\langle \Phi_K F_2 \Phi_L \rangle =$ $\langle p \xi_k(r_k) I_k^z q \rangle$	Category
$I (\Phi_K)$	$J (\Phi_L)$	Φ_K	Φ_L			
0	0	No excitation	No excitation	No excitation	$\langle h \xi_k(r_k) I_k^z h \rangle$	a
0	1	No excitation	$f_{i-} \rightarrow h_-$	$f_{i-} \rightarrow h_-$	$-\langle f_i \xi_k(r_k) I_k^z h \rangle$	c
0	2	No excitation	$h_+ \rightarrow e_{i+}$	$h_+ \rightarrow e_{i+}$	$\langle h \xi_k(r_k) I_k^z e_i \rangle$	c
0	3	No excitation	$f_{i-} \rightarrow e_{i-}$	$f_{i-} \rightarrow e_{i-}$	$-\langle f_i \xi_k(r_k) I_k^z e_i \rangle$	c
0	4	No excitation	$f_{i+} \rightarrow e_{i+}$	$f_{i+} \rightarrow e_{i+}$	$\langle f_i \xi_k(r_k) I_k^z e_i \rangle$	c
1	1	$f_{i-} \rightarrow h_-$	$f_{j-} \rightarrow h_-$	$f_{j-} \rightarrow f_{i-}$	$-\langle f_i \xi_k(r_k) I_k^z f_i \rangle$	c
1	2	$f_{i-} \rightarrow h_-$	$h_+ \rightarrow e_{i+}$	2e	0	b
1	3	$f_{i-} \rightarrow h_-$	$f_{j-} \rightarrow e_{i-}$	$i = j: h_- \rightarrow e_{i-}$ $i \neq j: 2e$	$-\langle h \xi_k(r_k) I_k^z e_i \rangle$ 0	c b
1	4	$f_{i-} \rightarrow h_-$	$f_{j+} \rightarrow e_{i+}$	2e	0	b
2	2	$h_+ \rightarrow e_{i+}$	$h_+ \rightarrow e_{k+}$	$e_{i+} \rightarrow e_{k+}$	$\langle e_i \xi_k(r_k) I_k^z e_k \rangle$	c
2	3	$h_+ \rightarrow e_{i+}$	$f_{i-} \rightarrow e_{k-}$	2e	0	b
2	4	$h_+ \rightarrow e_{i+}$	$f_{i+} \rightarrow e_{k+}$	$l = k: f_{i+} \rightarrow h_+$ $l \neq k: 2e$	$\langle f_i \xi_k(r_k) I_k^z h \rangle$ 0	c b
3	3	$f_{i-} \rightarrow e_{i-}$	$f_{j-} \rightarrow e_{k-}$	$i = j: e_{i-} \rightarrow e_{k-}$ $l = k: f_{j-} \rightarrow f_{i-}$ $l \neq j \text{ and } l \neq k: 2e$	$-\langle e_i \xi_k(r_k) I_k^z e_k \rangle$ $-\langle f_j \xi_k(r_k) I_k^z f_i \rangle$ 0	c c b
3	4	$f_{i-} \rightarrow e_{i-}$	$f_{j+} \rightarrow e_{k+}$	2e	0	b
4	4	$f_{i+} \rightarrow e_{i+}$	$f_{j+} \rightarrow e_{k+}$	$l = k: f_{j+} \rightarrow f_{i+}$ $l \neq j \text{ and } l \neq k: 2e$	$\langle e_i \lambda_k(r_k) I_k^z e_k \rangle$ $\langle f_j \lambda_k(r_k) I_k^z f_i \rangle$ 0	c c b

In the case of Fig. 3b, only one term is left; thus

$$\langle \Phi_K | F_2 | \Phi_L \rangle = \langle h_1 | \xi_k(r_k) I_k^z | h_1 \rangle. \quad [24]$$

(b'') *Double Excitation*

For the same reason mentioned in (b'), there is

$$\langle \Phi_K | F_2 | \Phi_L \rangle = 0.$$

(c'') *Single Excitation*

Assuming the same excitation given in Fig. 2 in (c'), we determine in the same way that [21] is left with only one term which is relevant with the excitation

$$\langle \Phi_K | F_2 | \Phi_L \rangle = \langle p_- | \xi_k(r_k) I_k^z S^z | q_- \rangle.$$

Separating the spin and orbital variables, we get

$$\langle \Phi_K | F_2 | \Phi_L \rangle = -S^z \langle p | \xi_k(r_k) I_k^z | q \rangle. \quad [25]$$

When extended to the general cases, $p_{\pm} \rightarrow q_{\pm}$, we have

$$\langle \Phi_K | F_2 | \Phi_L \rangle = \pm S^z \langle p | \xi_k(r_k) I_k^z | q \rangle. \quad [26]$$

All the possible matrix elements of $\langle \Phi_K | F_2 | \Phi_L \rangle$ are listed in Table 2.

Substituting $\langle \Phi_I | F_1 | \Phi_J \rangle$ and $\langle \Phi_K | F_2 | \Phi_L \rangle$ into [9], we get

$$\begin{aligned} P_0 \mathcal{H}_1 P_n \mathcal{H}_1 P_0 &= 2\beta H^z S^z \sum_{I,J,K,L} A_{0I} A_n J A_{nK} A_{0L} \\ &\quad \times \sum_k \langle p | l'^z | q \rangle_{(I,J)} \langle p' | \xi_k(r_k) I_k^z | q' \rangle_{(K,L)} \\ &= 2\beta H^z S^z \sum_k \sum_{I,J,K,L} A_{0I} A_n J A_{nK} A_{0L} \langle p | l'^z | q \rangle_{(I,J)} \\ &\quad \times \langle p' | \xi_k(r_k) I_k^z | q' \rangle_{(K,L)}. \end{aligned} \quad [27]$$

Equation [27] is a sum of atom k , and each term refers to one ξ_k only. In the same way we could write $P_0 \mathcal{H}_2 P_0$ as a sum of k ; then the whole right-hand side of Eq. [4] could be rewritten as the sum of k . According to Stone's argument,⁴ each k th term must be independently gauge-invariant, and we could put $\mathbf{d} = \mathbf{r}_k$, $\mathbf{l}' = \mathbf{l}_k$ for the k th term; therefore, the whole expression is gauge-invariant. Since the second-order perturbation term $P_0 \mathcal{H}_2 P_0$ is usually negligible compared with the first-order perturbation terms $P_0 \mathcal{H}_1 P_n \mathcal{H}_1 P_0$,⁵ we omit the tediously long but unnecessary treatment for $P_0 \mathcal{H}_2 P_0$, and put $\mathbf{l}' = \mathbf{l}_k$ directly for $P_0 \mathcal{H}_1 P_n \mathcal{H}_1 P_0$. The gauge-invariant expression for g^{zz} is then given by

⁴ See Eqs. [70] and [71] in Section 4 of Stone's paper (I).

⁵ See Section 6 of Stone's paper (I).

$$g^{zz} = 2 - \sum_{n \neq 0} \frac{h''(n)}{E_n - E_0}, \quad [28]$$

where

$$h''(n) = 2 \sum_{I,J,K,L} A_{0I} A_{nJ} A_{nK} A_{0L} \cdot \sum_k \langle p | l_k^z | q \rangle_{(I,J)} \\ \times \langle p' | \xi_k(r_k) l_k^z | q' \rangle_{(K,L)}.$$

The calculation of g^{zz} is usually based on the calculation of the matrix elements over basis functions of MOs,

$$\langle p | l_k^z | q \rangle \quad [29a]$$

and

$$\langle p' | \xi_k(r_k) l_k^z | q' \rangle. \quad [29b]$$

Express the MOs in terms of a linear combination of atomic orbitals,

$$|p\rangle = \sum_k |\chi_k^{(p)}\rangle \\ |q\rangle = \sum_k |\chi_k^{(q)}\rangle, \quad [30]$$

where χ_k is an atomic orbital on atom k (unnormalized). Substituting [30] into [29a], we obtain

$$\langle p | l_k^z | q \rangle = \sum_{k',k''} \langle \chi_k^{(p)} | l_k^z | \chi_{k'}^{(q)} \rangle. \quad [31]$$

We neglect overlap between orbitals on different atoms; that is, we ignore all terms in the sum [31] except those for which $k' = k''$, and therefore [31] can be rewritten as

$$\langle p | l_k^z | q \rangle = \sum_{k'} \langle \chi_k^{(p)} | l_k^z | \chi_{k'}^{(q)} \rangle. \quad [32]$$

Substitute [30] into [29b] to get

$$\langle p' | \xi_k(r_k) l_k^z | q' \rangle = \sum_{k',k''} \langle \chi_{k'}^{(p')} | \xi_k(r_k) l_k^z | \chi_{k''}^{(q')} \rangle. \quad [33]$$

Since $\xi(r)$ decreases rapidly with increasing r ($\xi(r) \sim 1/r^3$ for large r), we can treat $\xi(r)$ as effectively zero except near atom k ; therefore

$$\xi_k(r_k) = \begin{cases} 0 & r \gg r_k \\ \xi_k & r \leq r_k \end{cases}$$

where ξ_k is the usual spin-orbit coupling constant for atom k . Then [33] is replaced with

$$\langle p' | \xi_k(r_k) l_k^z | q' \rangle = \xi_k \langle \chi_k^{(p')} | l_k^z | \chi_k^{(q')} \rangle. \quad [34]$$

Substituting [32] and [34] into [28], we obtain

$$g^{zz} = 2 - 2 \sum_{n \neq 0} \times \sum_{I,J,K,L} A_{0I} A_{nJ} A_{nK} A_{0L} \\ \sum_{k,k'} \xi_k \langle \chi_k^{(p)} | l_k^z | \chi_{k'}^{(q)} \rangle_{(I,J)} \langle \chi_k^{(p')} | l_k^z | \chi_k^{(q')} \rangle_{(K,L)} \\ \times \frac{1}{E_n - E_0}. \quad [35]$$

The relationship between p , q and I , J is given in Table 1, while that of p' , q' and K , L is in Table 2.

g^{xx} and g^{yy} can be given by similar expressions.

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