A density functional investigation of the ground- and excited-state properties of ruthenocene

Claude Daul
Institut de Chimie Inorganique, Université de Fribourg, Pérolles, CH-1700 Fribourg, Switzerland

Hans-Ulrich Güdel
Institut für anorganische, analytische und physikalische Chemie, Universität Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland

Jacques Weber
Département de Chimie Physique, Université de Genève, 30 quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland

(Received 3 September 1992; accepted 20 November 1992)

Quantum chemical calculations based on density functional theory have been performed on ruthenocene. Excellent agreement is obtained with ground- and excited-state properties derived from optical spectroscopy. In particular, the energies of the first d-d excitations, the unusually large Stokes shift, the structural expansion of Ru(cp)₂ and the substantial reduction of the Ru-cp force constant in the first triplet excited state are almost quantitatively reproduced. The lowest-energy excitation is found to have substantial charge transfer character.

I. INTRODUCTION

Among the hundreds of known metalloccenes, those deriving from a 4d⁶ and 5d⁶ electron configuration have been shown to emit visible light upon ultraviolet (UV) excitation.¹,² And within these, the luminescence and excitation spectrum of Ru(cp)₂ has been studied in the greatest detail because it exhibits a long progression with a well resolved fine structure.³,⁴ Detailed information about the first excited state can therefore be derived from this spectrum. In particular, it was found that the structure of Ru(cp)₂ is significantly expanded in this nominally d-d excited state, with an increase of the vertical Ru-cp distance of 0.12–0.14 Å (see Fig. 1). The principal progression forming mode in the luminescence spectrum is the totally symmetric Ru-cp stretching vibration with a frequency of 333 cm⁻¹ in the electronic ground state. In a one-dimensional coordinate picture, the principal structural expansion of the excited state can therefore be represented as shown in Fig. 2. The long harmonic progression is characterized by a Huang–Rhys factor of ~15. The electronic origin is so weak that a crystal of several km thickness would be required to obtain an optical density of one! Nevertheless, by using highly selective laser spectroscopy, the origin region could be explored both in luminescence and excitation.⁵ From the measured vibrational frequencies the force constant of the Ru-cp stretching vibration was found to be reduced by 20% in the first excited state. There is some evidence in Ref. 3 that in crystalline Ru(cp)₂, there are some minor excited state distortions along some other coordinates. We neglect these and concentrate on the principal Ru-cp expansion in the present study.

The positions of the first excited triplet and singlet states are estimated from the absorption spectrum as 27 000 and 29 000–34 000 cm⁻¹, respectively.⁶ From x-ray diffraction the Ru-cp distance in the ground state is known to be 1.816 Å.⁶ These experimental data provide a very comprehensive and detailed basis for a quantum chemical investigation of the ground and excited states in ruthenocene. The first excited state of Ru(cp)₂ is one of the best characterized of any coordination compound.

There have been a number of quantum chemical studies of the molecular and electronic structure of metalloccenes, in particular of ferrocene.³,¹² In all of these the emphasis was placed on ground-state properties. Undoubtedly, as reported by one of us,⁷ ferrocene is an “enfant terrible” of quantum chemistry due to the difficulty to reproduce accurately such an important structural parameter as the vertical iron-ring distance. Indeed, ab initio calculations performed at the self-consistent field (SCF) level with good basis sets overestimate this parameter by as much as 0.23 Å,⁸ as compared with the experimental value 1.66 Å,⁹ and it is only when introducing correlation within the sophisticated modified coupled-pair functional (MCPF) approach that Park and Almlöf have obtained a satisfactory distance of 1.68 Å.¹⁰ Local-spin density (LSD) methods, however, lead to structural predictions in better agreement with experiment with metal-ring distances of 1.60 and 1.58 Å in the LCGTO-Xα (Ref. 11) and LCGTO-LSD (Ref. 7) approximations, respectively. In addition to these structural studies, a great many ab initio and semiempirical investigations have been carried out on the characteristics of chemical bonding and spectroscopic properties of ferrocene.¹² This is in contrast to other members of the metalloocene series for which few theoretical studies have been performed, specially for the 4d- and 5d-transition metal systems.

In the present work, we report the results of a theoretical investigation performed on ruthenocene, with a particular emphasis placed on excited-state properties which can be compared with experimental results. The linear combination of Gaussian type orbitals (LCGTO) LSD model developed by St-Amant and Salahub¹³ has been used to this end, as LSD techniques have been recently shown to lead to accurate predictions for the structure and properties of organometallic compounds.¹⁴-¹⁶ The energies of the excited
II. COMPUTATIONAL METHODS

A. Density functional calculations

The linear combination of Gaussian-type orbitals—
model core potential—density functional (LCGTO-MCP-
DF) method\(^{17-19}\) and its corresponding DEMON program
package\(^{20}\) have been used. In all the calculations, the
Vosko-Wilk-Nusair LSD exchange-correlation potential
was employed\(^{21}\) and all the core and valence electrons were
explicitly taken into account, i.e., the MCP option has not
been applied. The one-electron (orbital) basis set used in
the calculation has been specially optimized for
\(\sim 1000\)
\(\sim 20000\) \(\sim 0-0\) transition (origin)
\(\Delta = 0.12 - 0.14 \text{ Å}\)

FIG. 1. Structural model of the ruthenocene molecule.

LCGTO-DF calculations by Godbout and Andzelm.\(^{22}\) It is
of double-zeta plus polarization quality, the contraction
pattern being Ru (63321/53211/531), C (62114111), H
(41/1), which leads in the usual six-component \(d\)-type
Cartesian Gaussian functions to a basis set of dimension
239. The auxiliary basis sets required by the LCGTO-DF
model to fit the electron density and the exchange-
correlation potential\(^{20}\) have been chosen as Ru (5,5;5,5), C
(4,3;4,3), and H (3,1;3,1).\(^{22}\)

The initial geometry of ruthenocene was taken from
the x-ray diffraction study of Seiler and Dunitz,\(^6\) with cy-
clopentadienyl rings lying in parallel planes and in an
eclipsed conformation (\(D_{sh}\) symmetry, Fig. 1). In our first
calculation, the bond distances are therefore the following:
Ru–C=2.186 Å, C–C=1.430 Å, and C–H=1.100 Å, this
latter value being taken by analogy from the electron-
diffraction measurements performed by Haaland\(^9\) on fer-
rocene. These structural data correspond to a vertical
metal-ring distance \(d_{Ru-cp}\) of 1.816 Å. Then, in further cal-
culations attempting to optimize this parameter for both
ground and excited states, both C–C and C–H distances
were kept at their initial values and only \(d_{Ru-cp}\) was varied.

B. Multiplet structure

The calculation of the multiplet structure (MS) splittings
in DF theory has been previously discussed by Zie-
gler et al.\(^{23}\) According to these authors, it is possible to
replace the energy of a single determinant by the corre-
sponding statistical energy as obtained in DF theory. The
energy of a multiplet arising from a given configuration
being a weighted sum of single-determinantal energies, it is
thus possible to obtain the multiplet splittings.

Following this line of thought we used symmetry based
arguments to rationalize the relation between the multiplet
splittings and single-determinantal energies resulting from
DF calculations. A system of computer programs working
on both mainframe or personal computers has been devel-
oped yielding these relations for any desired point group. A
short outline of the method is given in the Appendix.

It is known that in \(D_{sh}\) metallocenes the \(nd\) orbitals of
metal split into \(e_g, a_l\), and \(e_u\) molecular orbitals (MOs)
characterized by the energy ordering \(e_g < a_l < e_u\).\(^{24}\) As ru-
thenocene is a \(4e_g\) system, the ground state (GS)
configuration is

\[ |(3e_g)^4(5a_l)^2(4e_u)^0\rangle, \]

(1)

Furthermore, when considering singly excited triplet states
only, we have

\[ |(3e_g)^4(5a_l)^1(4e_u)^1\rangle, \]
\[ |(3e_g)^3(5a_l)^2(4e_u)^0\rangle, \]
\[ |(3e_g)^3(5a_l)^1(4e_u)^1\rangle, \]
\[ |(3e_g)^2(5a_l)^2(4e_u)^1\rangle. \]

(2)

Applying the model described in the Appendix, we obtain
the following energy matrices. That is a \(2 \times 2\) matrix cor-
responding to \(3E_u\), where the first entry represents the
\(5a_l \rightarrow 4e_u\) excitation and the second one the \(3e_g \rightarrow 4e_u\)
excitation, respectively.

FIG. 2. Low-temperature luminescence spectrum of ruthenocene
(adapted from Ref. 3) and corresponding configurational coordinate
diagram along the principal distortion coordinate.
TABLE I. Ground-state orbital energies and corresponding charge distribution\(^a\) calculated for the upper valence MOs of Ru(cp)\(_2\) (\(d_{Ru-cp} = 1.816 \text{ Å}\)).

<table>
<thead>
<tr>
<th>Orbital energy (eV)</th>
<th>$\text{occ.}(^b)</th>
<th>$\text{Ru}</th>
<th>C</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$s$</td>
<td>$p$</td>
<td>$d$</td>
<td>$s$</td>
</tr>
<tr>
<td>$3e_2^o$</td>
<td>0.24</td>
<td>0</td>
<td>85</td>
<td>96</td>
</tr>
<tr>
<td>$6a_1^o$</td>
<td>0.04</td>
<td>51</td>
<td>49</td>
<td>3</td>
</tr>
<tr>
<td>$4e_1^o$</td>
<td>0.92</td>
<td>2</td>
<td>88</td>
<td>4</td>
</tr>
<tr>
<td>$5a_1^o$</td>
<td>4.57</td>
<td>4</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>$3e_2$</td>
<td>5.17</td>
<td>4</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>$4e_1^o$</td>
<td>6.09</td>
<td>4</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>$3e_1^o$</td>
<td>7.40</td>
<td>4</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>$4a_1^o$</td>
<td>9.00</td>
<td>2</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>$2e_2^o$</td>
<td>9.19</td>
<td>4</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>$2e_2^o$</td>
<td>9.27</td>
<td>4</td>
<td>77</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)The calculation of the charge distribution has been performed using a Mulliken population analysis.

\(^b\)Occupation number of each MO.

The $d$ population analysis on ruthenium has been performed on the basis of six-component Cartesian functions; the C and H charge distributions refer to all the respective atoms of the same type.

We estimate $B = 400 \text{ cm}^{-1}$, the free ion value being 474 cm\(^{-1}\). The value chosen for this parameter is not critical as modifying it by a factor of 2 does not significantly affect the results.

II. RESULTS AND DISCUSSION

A. Ground-state electronic structure

The orbital energies and corresponding charge distributions of the upper valence MOs of the \([1\text{A}]_1(3e_2^o(5a_1^o)^4(4e_1^o)^0)\) ground state of ruthenocene, calculated for \(d_{Ru-cp} = 1.816 \text{ Å}\), are presented in Table I. It is seen that, as expected for a member of the metallocenes series, the calculated sequence of predominantly metal 4$d$ orbitals is $3e_2^o(4d) < 5a_1^o(4d) < 4e_1^o(4d\pi)$ for this formally $d^8$ compound. The metal 4$d$ contributions to these MOs differ significantly. The strongly antibonding $4e_1^o$ MO exhibits an important delocalization (49\%) on the ligand rings, whereas $3e_2^o$ is slightly bonding and $5a_1^o$ essentially nonbonding, both with predominant metal 4$d$ character (more than 80\%). The main features of these MOs and in particular their percentage of metal character are very similar to those obtained in previous LSD calculations performed for other metallocenes such as ferrocene\(^{25}\) or cobaltocene\(^{26}\), the major characteristic being that in all the cases $4e_1^o$ shows much more delocalization on the ligands than $3e_2^o$ or $5a_1^o$. This indicates that an adequate ligand field description of the $d-d$ excited states should be based on a model taking account of the very different covalency reduction factors of these orbitals (see below).

Coming back to Table I, it is seen that below the $3e_2^o$ MO one finds the typical ligand $\pi$ orbitals $4e_1^o$, $3e_2^o$, and $4a_1^o$. As expected,\(^{26}\) most of the covalent metal–ligand interactions in ruthenocene occur through the $3e_2^o$ MO which is strongly bonding with a large admixture of metal 4$d\pi$ to ligand $p$ orbitals. The bonding character of this MO is underlined by its large percentage (30\%) of metal 4$d$ contribution, suggesting that a significant $\pi$ ligand-to-...
metal charge donation occurs. Table I reveals that the amount of metal-to-ligand back-bonding charge transfer arising through the $5e^\pi$ and $3e^\pi$ MOs is much smaller. It is therefore not surprising that our calculations finally lead to a gross charge of $+0.40$ on ruthenium, which again compares rather well with the $+0.76$ charge on iron calculated previously for ferrocene. As expected, at lower energies than these typical ligand $p\sigma$ orbitals, one observes the presence of the ring $p\sigma$ orbitals which are generally characterized by their very small, if any, metal contributions.

The virtual MOs of ruthenocene are of utmost importance in this work as they will be used to generate the electronic configurations of the excited states. At higher energies than the $4e^\gamma$ lowest unoccupied molecular orbital (LUMO), one finds $6a_{1}$, which is a typical Rydberg MO with Ru $5s$ character, and $3e^\gamma$, the first partner of the ligand $2p\pi^*$ MOs. As the energy difference between each of these MOs and the $4e^\gamma$ orbital is of the order of $1$ eV, one can probably expect that they will lead to Rydberg and metal-to-ligand excited states, respectively, lying at higher energies than the $d-d$ transitions we are interested in and, consequently, that we can discard them in the calculation of metal-centered excited states. The same conclusion also applies to excited states resulting from $4e_1^\gamma - 4e_2^\gamma$ ligand-to-metal transitions. We will therefore concentrate on the $d-d$ transitions in the calculation and interpretation of the low-energy absorption and emission spectrum of ruthenocene.

**B. Potential energy curves of the ground and triplet excited states**

As mentioned above, the vertical metal-ring distance in metallocenes, particularly in ferrocene, is a very difficult parameter to reproduce by *ab initio* quantum chemical calculations. It was therefore of particular interest to optimize the $d_{Ru-cp}$ distance in the ruthenocene ground state using the present LCGTO-DF model, and the results are presented in Tables II and III and Fig. 3. It is seen that the calculations lead to a very good agreement with the x-ray diffraction data, the predicted distance being only $0.017$ Å shorter than the $1.816$ Å experimental result. The quality of the LCGTO-DF prediction for ruthenocene is therefore perfectly in line with similar results previously obtained using the same technique for organic molecules, which showed that bond lengths are generally predicted within $\pm 0.02$ Å better compared with experiment.

When comparing both Hartree-Fock and LSD calculations performed for ferrocene and examining the present result obtained for ruthenocene, one may therefore deduce, in agreement with the previous conclusion of Andzelm and Wimmer, that the LCGTO-DF model incorporates a treatment of electron correlation roughly equivalent to that of second-order Möller-Plesset theory.

Finally, one might wonder why our structural prediction of $d_{Ru-cp}$ is significantly better than that obtained for $d_{Fe-cp}$ in ferrocene using the same LCGTO-DF model and a one-electron basis set of similar quality. Whereas the reason for this difference is still not completely clear, we suggest that the optimization of the LSD basis set for iron

**TABLE III. Comparison between experimental and calculated (LCGTO-LSD without MS) ground- and excited-state properties of ruthenocene.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Expt</th>
<th>Calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1_A1 \rightarrow 3E_1$ absorption maximum (cm$^{-1}$)</td>
<td>27 000$^a$</td>
<td>26 900</td>
</tr>
<tr>
<td>$3E_1 \rightarrow 1A_1$ emission maximum (cm$^{-1}$)</td>
<td>17 000$^b$</td>
<td>19 000</td>
</tr>
<tr>
<td>$1A_1 \rightarrow 1E_{1/2}$ absorption (cm$^{-1}$)</td>
<td>29 000-34 000$^a$</td>
<td>28 300-32 000</td>
</tr>
<tr>
<td>Ru-cp distance ground state (GS) (Å)</td>
<td>1.816$^c$</td>
<td>1.799</td>
</tr>
<tr>
<td>Ru-cp distance excited state (ES) (Å)</td>
<td>1.94-1.96$^b$</td>
<td>1.94</td>
</tr>
<tr>
<td>Ru-cp force constants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f(GS)$</td>
<td>1.25$^d$</td>
<td>1.35</td>
</tr>
<tr>
<td>$f(ES)$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Estimated from Ref. 2.
$^b$References 1 and 3.
$^c$Reference 6.
$^d$Reference 4.
has not been performed using the same criteria as that of ruthenium.\textsuperscript{20}

We now turn to the results obtained for the triplet excited states resulting from the \((3\epsilon_j')^4(5\alpha_j')^1(4\epsilon_i')^1\) and \((3\epsilon_j')^3(5\alpha_j')^2(4\epsilon_i')^1\) configurations which may be qualified as typical ligand-field states arising from \(d-d\) transitions. It is well known that, being a one-electron model, the LCGTO-DF method takes only partial account of the multiplet structure inherent to excited configurations with several open shells; performing spin-polarized (SP), or spin-unrestricted, calculations does split up the different spin multiplets, but not the various orbital multiplets resulting from such electronic configurations.\textsuperscript{50} In the present case and taking only the triplets into consideration, the \((3\epsilon_j')^4(5\alpha_j')^1(4\epsilon_i')^1\) configuration leads to a single triplet \(3E'_1\), but the \((3\epsilon_j')^3(5\alpha_j')^2(4\epsilon_i')^1\) configuration generates both \(3E'_1\) and \(3E'_2\) excited states. This means that SP-LCGTO-DF calculations will not be able to split up the \(3E'_1\) and \(3E'_2\) states generated in the latter case nor to describe configuration interaction (CI) effects between both \(3E'_1\) states arising from these configurations. However, such interactions may be taken into account by using the LCGTO-DF-MS procedure outlined above (see Sec. II B).

In a first step, we have therefore carried out SP-LCGTO-DF calculations on these excited configurations. In order to keep an electronic structure with \(D_{5h}\) symmetry, these calculations have been performed by always forcing the two components of degenerate open shell orbitals to be equally populated by a fractional number of electrons, i.e., by placing 0.5 \(e\) in the two components of \(4\epsilon_i''\) in \(T_1\) and \(T_2\), and 1.5 \(e\) in the two components of \(3\epsilon_j'\) in \(T_2\). In a second step, we have used the LCGTO-LSD-MS model to evaluate the energies of the first triplet excited states. The results of these calculations are presented in Table II.

Examination of Table II shows that, as expected, the results obtained for the \(T_2\) triplet are equal to those calculated for the \(3E'_2\) excited state. Indeed, this \(3E'_2\) triplet state is the only one generated within the singly excited \(d-d\) manifold. A second conclusion which emerges from inspection of Table II is that the MS calculations lead to small modifications of the first-order single-determinant predictions (compare \(T_1\) vs the two \(3E'_1\) results). Indeed, without inclusion of these second-order MS effects, the two triplets \(3E''_1\) and \(3E''_2\) stemming from the \((3\epsilon_j')^3(5\alpha_j')^1(4\epsilon_i')^1\) configuration are accidentally degenerate. Similarly, the position of the minima of the potential energy curves calculated as a function of \(d_{Ru-cp}\) are almost equal for \(T_1\) and the lower \(3E'_1\) triplet and for \(T_2\) and both \(3E'_2\) and the upper \(3E'_1\) triplet, respectively. This shows again that, in the present case, MS effects do not significantly modify the single-determinant description of the excited states.

It is known that, from a purely theoretical point of view, excited states are difficult to handle in DF theory because (i) the Hohenberg–Kohn theorems are in principle valid only for a ground-state electron density and (ii) as in any Hartree–Fock based model, there is the orthogonality problem of the excited state wave function to the ground state one.\textsuperscript{31} However, recent results have shown that, provided a local potential capable to simultaneously describe the ground and excited states with similar accuracy is used, DF models may represent a valuable alternative to traditional CI approaches to evaluate the properties of excited states.\textsuperscript{32,33} As no such investigations have yet been carried out for large systems such as ruthenocene, it was therefore interesting to apply the present LCGTO-DF model to evaluate the energies and potential energy curves of the excited triplets, both with and without calculation of the multiplet structure.

The results are summarized and compared with experiment in Table III and Fig. 3. The overall agreement is excellent. Not only the absolute transition energies, but also the unusually large Stokes shift, the geometrical expansion in the excited state and the reduction in the force constant are very well reproduced. To our knowledge there are no other examples of heavy metal complexes for which so many ground- and excited-state parameters have been determined both experimentally and by quantum chemistry calculations. It is therefore not possible to decide whether the excellent agreement found here is simply fortuitous or whether the density functional approach is intrinsically better suited for the calculation of excited state properties than other techniques. Our result is certainly...
promising, and calculations on other systems are needed to test the general validity of the theoretical approach. However there are not many transition metal complexes for which excited states have been characterized as accurately as for Ru(cpf)_2.

The large geometrical expansion of Ru(cpf)_2 in the luminescent state which leads to the typical and unusually long progression in the spectrum can be easily understood in terms of orbital occupancies. As the excited states result from an electronic excitation to the 4e'' MO, which is strongly antibonding, it is not surprising that they are characterized by a significant increase of the Ru-cp distance. In addition, the slight differences in the position of the minima exhibited by the curves of the excited states are to be related to the different characteristics of the 3e_2 and 5a_1' MOs, the former being somewhat more bonding than the latter one. The accepting orbital 4e'' has ~50% Ru 4d and 50% ligand p\pi character. The lowest-energy excitations in Ru(cpf)_2 are thus d-d transitions with a strong admixture of metal-to-ligand charge transfer character.

APPENDIX

In the case of symmetrical molecules with degenerate orbitals, the multiplets arising from an open-shell configuration can no longer be expressed by a single determinant. That is, DF calculations do not yield multiplet energies directly. Symmetry consideration is therefore needed. Actually, the use of symmetry will not only enable us to perform such calculations, but also to simplify the problem considerably as will be described below.

The multiplet wave functions

\[ \psi_i = |\alpha \Gamma_m S m_S \rangle \]  

(A1)

arising from a given open-shell configuration \( \alpha \), are easily obtained by vector coupling as

\[ \psi_i = \sum C_{i\mu} \phi_{\mu} \]  

(A2)

where \( \Gamma \) is the label of the irreducible representation of the spatial part of the wave function, \( m_T \) refers to its component in case of degeneracy, \( S \) is the spin part of the wave function with component \( m_S \) when the spin multiplicity is larger than 1; \( \phi_{\mu} = |X_1X_2X_3...\rangle \) is a single-determinantal wave function of spin-orbitals \( X_1, X_2, X_3... \) and \( C_{i\mu} \) is an orthogonal square matrix of symmetry coefficients. Let us note that DF or Hartree–Fock calculations provide directly the energies associated with \( \phi_{\mu} \) as barycenters of the various energies resulting from the states generated by the corresponding configurations. On the other hand, this energy \( E(\phi_\mu) \) can also be obtained from Slater's rules for a single determinant,\(^{35}\) i.e.,

\[
E(\phi_\mu) = \sum_{i<j} \left[ \int \chi_i^\ast (1) \chi_j^\ast (2) G_{12} \chi_i (1) \chi_j (2) \, dv_1 \, dv_2 - \int \chi_i^\ast (1) \chi_j^\ast (2) G_{12} \chi_j (1) \chi_i (2) \, dv_1 \, dv_2 \right]
\]

\[
= \sum_{i<j} \left[ \langle \chi_i | \chi_j \rangle - \langle \chi_j | \chi_i \rangle \right],
\]

(A3)

where \( G_{12} = 1/r_{12} \) as a sum of Coulomb and exchange integrals. These electrostatic integrals can in turn be expressed, using coupling coefficients and reduced matrix elements, as follows:\(^{34}\)

\[
\langle \alpha \gamma (1) \beta \delta (2) | G | \epsilon \gamma (1) d \delta (2) \rangle
\]

\[
= \sum_{i \neq \phi} \langle \alpha \gamma (1) | g_{1\phi}^{(1)} | \epsilon \gamma (1) \rangle \langle \beta \delta (2) | g_{1\phi}^{(2)} | d \delta (2) \rangle
\]

\[
= \sum_{\phi} \sqrt{\frac{a}{\alpha \gamma \beta \delta} \phi} \sum_i \langle a || g_{1\phi}^{(1)} || c \rangle \langle b || g_{1\phi}^{(2)} || d \rangle,
\]

(A4)

where \( a, b, c, d, f \) denote iridium representations and \( \alpha, \beta, \gamma, \delta, \phi \) denote components, assumed real. The coupling coefficients (Griffith's V-coefficients\(^{34}\)) are the same for all values of \( i \), and the sum over \( i \) on the right-hand side can be considered as a single reduced electrostatic matrix element related through Eq. (A3) to \( E(\phi_\mu)'s. \)

The state energies we seek are thus obtained as

\[
\langle \psi_\mu | G | \psi_j \rangle = \sum_{\mu, \nu} C_{\mu\nu} C_{\nu\psi} \langle \phi_\mu | G | \phi_j \rangle
\]

(A5)

expressed in terms of electrostatic matrix elements over single determinants. These latter expressions are then calculated using Slater's rules as a function of two-electron integrals, which in turn are expressed in terms of the minimal number of reduced electrostatic matrix elements, each of them requiring an individual DF calculation.

This whole scheme yields a contracted expression of state energies \( E(\psi_\mu) \) as a function of DF configurational energy barycenters \( E(\phi_\mu) \).

Unfortunately this procedure yields only Coulomb \( (l|j) \) and exchange \( (i|j) \) contributions, i.e., first-order electrostatic interactions contributing to the diagonal term [cf. Eq. (A3) for the notation; \( i \) and \( j \) refer to MO indices]. Second-order, off-diagonal, contributions depend upon \((i|k)\) elements which are neither of Coulomb nor of exchange type and which can therefore not be obtained from the single-determinant energies \( E(\phi_\mu) \). Thus, in cases where second order electrostatic interaction is important, the off-diagonal two-electron integrals have to be calculated explicitly from the SCF wave functions or approximated by appropriate model calculations. For ruthenocene, e.g., second order interaction is important (cf. Sec. II B).

ACKNOWLEDGMENTS

The authors are grateful to Professor D. Salahub for providing a copy of the DEMON program and to Dr. A. Goursot and Dr. I. Papai for fruitful discussions. This work is part of Projects 20-29001.90, 20-29585.90, and 20-29856.90 of the Swiss National Science Foundation.

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22N. Godbout and J. Andzelm (to be published). A listing of both orbital and auxiliary basis sets used in the present calculations is available upon request.