Derivation of a formula for the resonance integral for a nonorthogonal basis set

(structure/calculation of magnetic circular dichroism molecules)

YUNG-CHANG YIM AND HENRY EYRING*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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ABSTRACT In a self-consistent field calculation, a formula for the off-diagonal matrix elements of the core Hamiltonian is derived for a nonorthogonal basis set by a polyatomic approach. A set of parameters is then introduced for the repulsion integral formula of Mataga–Nishimoto to fit the experimental data. The matrix elements computed for the nonorthogonal basis set in the π -electron approximation are transformed to those for an orthogonal basis set by the Löwdin symmetrical orthogonalization.

Semiempirical calculations using the Hartree–Fock equation (1) with a zero differential overlap (2–7) neglect the overlap integrals and assume orthogonality of a set of atomic orbitals. These approaches have been rationalized through the use of the Löwdin orthogonalized atomic orbital (8). Explanations of the earlier Pariser–Parr method (2–4) have been given by Gladney (9), Fischer–Hjalmars (10), Berthier *et al.* (11), and several other authors (12–14); a systematic treatment of the zero differential overlap assumption using the nonorthogonal atomic orbitals has been compared with the procedure using the nonorthogonal Löwdin atomic orbitals by Fischer–Hjalmars (15–18); and further application of the orthogonal transformation has been carried out by Adams and Miller (19, 20). Linderberg (21, 22) has shown that the equivalence of the dipole length and velocity form of oscillator strength places a condition on the parameters used in the Pariser–Parr model. For the case of two orbitals centered at positions A and B and having a vanishing gradient perpendicular to the axis connecting them, Linderberg has derived Eq. 1.

$$\beta_{\mu\nu} = \frac{\hbar^2 L}{m R_{\mu\nu}} \frac{\partial S_{\mu\nu}}{\partial R_{\mu\nu}}, \quad [1]$$

where ϕ_μ and ϕ_ν are the atomic orbitals on atoms A and B, $S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$, $\bar{R}_{\mu\nu} = (\bar{R}_\mu - \bar{R}_\nu)$, and $\beta_{\mu\nu}$ is a resonance integral between the orbitals ϕ_μ and ϕ_ν . This procedure is a diatomic approach and neglects the higher order corrections that would occur in polyatomic molecules. There is not, however, a proper limit when B approaches A in this formula. To compute α , for the diagonal matrix elements of the core Hamiltonian, one needs to know β values for the nonorthogonal basis set, but we now only have β values for the orthogonal basis set, as given by Eq. 1. The β values for the nonorthogonal basis set can be obtained by the procedure described below.

Derivation of the off-diagonal matrix element of the core Hamiltonian

The fundamental equations for the self-consistent field method are

$$\begin{aligned} FC &= ESC, \\ |F - ES| &= 0, \\ \hat{C}_i S C_j &= \delta_{ij}, \end{aligned} \quad [2]$$

where F is the Fock matrix, E is the eigenvalue matrix of F , C is the eigenmatrix of F , δ_{ij} is the Kronecker delta, and S is the overlap matrix. The zero differential overlap approximation leads to the familiar contradiction of neglecting the overlap integral on the one hand and taking a nonzero value of the resonance integral on the other hand.

The Löwdin orthogonalized atomic orbitals and the Mulliken approximation (23) can be combined into a computational method in a self-consistent field calculation. The nonorthogonal orbitals, ψ_s , are transformed into the orthogonalized orbitals, ϕ_s , by the relationship

$$\phi = \psi S^{-1/2}. \quad [3]$$

Now, the new Fock matrix will be given by

$$\begin{aligned} F^\lambda &= S^{-1/2} F S^{-1/2} \\ S^{-1/2} C &= C^\lambda. \end{aligned} \quad [4]$$

The quantities with the superscript λ are the matrices for the orthogonal basis set. The matrix elements of the Fock operator are then given by

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_{\sigma,\rho} Q_{\sigma\rho} (\langle \mu\nu | \sigma\rho \rangle - \frac{1}{2} \langle \mu\sigma | \nu\rho \rangle) \quad [5]$$

$$H_{\mu\nu}^{\text{core}} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 + \sum_c U_c \right| \nu \right\rangle,$$

where $Q_{\sigma\rho} = 2 \sum_i^{\text{occ}} C_{\sigma i} C_{\rho i}$ and U_i is the effective potential of atom c without its electron, as described by an atomic orbital χ_σ . U_i may be approximated as

$$U_c = U_c^* - Z_c \int \chi_\sigma^2 \chi_\sigma^2 \left(\frac{1}{r_{12}} \right) d\tau_{12}, \quad [6]$$

which is known as the Goeppert–Mayer and Sklar expansion (24). Here Z_c is the formal charge of atom c , and U_c^* is the potential of the neutral atom—i.e., the penetration potential. Now, the diagonal matrix elements of the core Hamiltonian will be given by

$$\begin{aligned} H_{\mu\mu}^{\text{core}} &= \langle \mu | -\frac{1}{2} \nabla^2 + U_a^* | \mu \rangle - Z_a \langle \mu\mu | \mu\mu \rangle \\ &- \sum_{c \neq a} Z_c \langle \mu\mu | \sigma\sigma \rangle + \sum_{c \neq a} U_{c,\sigma\sigma}^* \\ &\cong - (A_a + Z_a \gamma_{\mu\mu}) \sum_{c \neq a} Z_c \gamma_{\mu\sigma} \end{aligned} \quad [7]$$

where A_a is the electron affinity of atom a , $|\gamma_{\mu\sigma} = \langle \mu\mu | \sigma\sigma \rangle$, and

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Abbreviation: eV, electron volts.

* To whom reprint requests should be addressed.

the penetration integrals are neglected except for $U_{a,\mu\mu}^*$.

The Heisenberg equation of motion (25) for the position vector is

$$\vec{p} = \left(\frac{im}{\hbar} \right) [h, \vec{r}]. \quad [8]$$

Then, one may write

$$\frac{\hbar^2}{m} \vec{\nabla} = [\vec{r}, h] \quad [8a]$$

$$\tilde{\Omega} \equiv \frac{\hbar^2}{m} \vec{\nabla} \quad [9]$$

$$\tilde{\Omega}_{\mu\mu\nu} = \langle \chi_\mu | [\vec{r}, h] | \chi_\nu \rangle. \quad [9]$$

The Dirac (26) resolution of identity (Eq. 8a) for the nonorthogonal set would be

$$\sum_{\mu, \nu} \left| \chi_\mu \right\rangle S_{\mu\nu}^{-1} \left\langle \chi_\nu \right| = 1. \quad [10]$$

Using Eqs. 9 and 10, one obtains

$$\Omega = rs^{-1}h - hs^{-1}r \quad [11]$$

$$[(Rh - hR)/2] + \sum_{\sigma, \rho} (SRSh - hs^{-1}RS)/2. \quad [12]$$

Taking only two atomic orbitals as a basis set, one can write

$$\tilde{\Omega}_{\mu\nu} = (1 - S_{\mu\nu})^{-1} (R_\mu - R_\nu) \left[h_{\mu\nu} - \frac{S_{\mu\nu}}{2} (h_{\mu\mu} + h_{\nu\nu}) \right]. \quad [13]$$

From Eq. 13 one realizes that $\beta, h_{\mu\nu}$ cannot be approximated by $h_{\mu\nu} = (S_{\mu\nu}/2) (h_{\mu\mu} + h_{\nu\nu})$. Obviously, the left-hand side is not zero if $\mu \neq \nu$ and, therefore, the right-hand side is not zero. Accordingly, a straightforward Mulliken approximation with symmetrical orthogonalization cannot give the nonvanishing β values.

Rearranging Eq. 13 leads to

$$h_{\mu\nu} = \frac{\hbar^2}{m} [1 - S_{\mu\nu}^2] \tilde{R}_{\mu\nu} \cdot (\tilde{\nabla}_{\mu\nu}/R_{\mu\nu}^2) + S_{\mu\nu} (h_{\mu\mu} + h_{\nu\nu})/2 \quad [14]$$

$$= \frac{\kappa}{2} (h_{\mu\mu} + h_{\nu\nu}) S_{\mu\nu}$$

$$\kappa = 1 + \frac{\hbar^2}{m} (1 - S_{\mu\nu}^2) \tilde{R}_{\mu\nu} \cdot \tilde{\nabla}_{\mu\nu} - \left[\frac{S_{\mu\nu}}{2} (h_{\mu\mu} + h_{\nu\nu}) \right]^{-1}, \quad [15]$$

where

$$\tilde{R}_{\mu\nu} = \vec{R}_\mu - \vec{R}_\nu \text{ and } R_{\mu\nu} = |\tilde{R}_{\mu\nu}|. \quad [16]$$

For the polyatomic case, expansion of Eq. 12 in powers of S' ($S = I + S'$) gives

$$h_{\mu\nu} = \frac{\hbar^2}{m} (1 - S_{\mu\nu}^2) \tilde{R}_{\mu\nu} \cdot (\tilde{\nabla}_{\mu\nu}/R_{\mu\nu}^2) + \frac{1}{2} S_{\mu\nu} (h_{\mu\mu} + h_{\nu\nu}) \quad [17]$$

$$+ \frac{1}{2} (1 - S_{\mu\nu}^2) \tilde{R}_{\mu\nu} \cdot \left\{ \sum_{i \neq \mu, \nu} h_{\mu i} S_{i\nu} \tilde{R}_{i\nu} / (1 - S_{i\nu}^2) \right.$$

$$\left. - h_{\nu i} S_{i\mu} \tilde{R}_{i\mu} / (1 - S_{i\mu}^2) \right\} / R_{\mu\nu}^2$$

Substituting the $h_{\mu\nu}$ of Eq. 17 into itself and neglecting higher order terms, one obtains

$$h_{\mu\nu} = (1 - S_{\mu\nu}^2) B_{\mu\nu} + \frac{1}{2} S_{\mu\nu} (h_{\mu\mu} + h_{\nu\nu})$$

$$+ \frac{1}{2} \sum_{i \neq \mu, \nu} (1 - S_{\mu\nu}^2) \{ [(\tilde{R}_{\mu\nu} \cdot \tilde{R}_{i\nu}) S_{i\nu} B_{\mu i}$$

$$+ (\tilde{R}_{\mu\nu} \cdot \tilde{R}_{i\mu}) S_{i\mu} B_{\nu i}] / R_{\mu\nu}^2 + \frac{1}{2} S_{\mu i} h_{ii} S_{i\nu} \}$$

$$= \varepsilon_{\mu\nu} + \frac{1}{2} S_{\mu\nu} (h_{\mu\mu} + h_{\nu\nu}). \quad [18]$$

When $\beta_{\mu\nu} \equiv (\hbar^2/m) \tilde{R}_{\mu\nu} \cdot \tilde{\nabla}_{\mu\nu} / R_{\mu\nu}^2$,

$$h_{\mu\nu}^\lambda = \sum_{\rho, \sigma} S_{\mu\rho}^{-1/2} \varepsilon_{\rho\sigma} S_{\sigma\nu}^{-1/2} + (S^{1/2} H^o S^{-1/2}$$

$$+ S^{-1/2} H^o S^{1/2})_{\mu\nu} / 2, \quad [19]$$

Where H^o is the diagonal matrix of the core Hamiltonian. For the orthogonal basis, the repulsion integrals are given by

$$\langle \mu\nu | \sigma\rangle^\lambda = \langle \mu\mu | \sigma\sigma \rangle^\lambda \delta_{\mu\nu} \delta_{\sigma\rho}$$

$$= \sum_{p, q} (S_{\mu p}^{-1/2} S_{\mu p}^{1/2}) \gamma_{pe} (S_{\sigma q}^{-1/2} S_{\sigma q}^{1/2}) \delta_{\mu\nu} \delta_{\sigma\rho} \gamma_{\mu\nu}$$

$$= \sum C_{\mu p} \gamma_{pq} C_{q\nu} (C_{\mu p}; \equiv S_{\mu p}^{-1/2} S_{\mu p}^{1/2}). \quad [20]$$

To obtain Eq. 20 we used the Mulliken approximation.

For a benzene molecule, one obtains the following relationships (4):

$$E(^1E_{1u}) = -2(\beta_{12}^\lambda - \beta_{14}^\lambda) + 2k_1 - k_3 \quad [21]$$

$$E(^1B_{1u}) = -2(\beta_{12}^\lambda - \beta_{14}^\lambda) - k_2 + 3k_3 \quad [22]$$

$$E(^1B_{2u}) = -2(\beta_{12}^\lambda - \beta_{14}^\lambda) + k_2 - k_3 \quad [23]$$

$$E(^3B_{1u}) = -2(\beta_{12}^\lambda - \beta_{14}^\lambda) - k_2 - k_3, \quad [24]$$

where

$$k_0 = (\gamma_{11}^\lambda + 2\gamma_{12}^\lambda + 2\gamma_{13}^\lambda + \gamma_{14}^\lambda)/6 \quad [25]$$

$$k_1 = (\gamma_{11}^\lambda + \gamma_{12}^\lambda - \gamma_{13}^\lambda - \gamma_{14}^\lambda)/6 \quad [26]$$

$$k_2 = (\gamma_{11}^\lambda - \gamma_{12}^\lambda - \gamma_{13}^\lambda + \gamma_{14}^\lambda)/6 \quad [27]$$

$$k_3 = (\gamma_{11}^\lambda - 2\gamma_{12}^\lambda + 2\gamma_{13}^\lambda - \gamma_{14}^\lambda)/6. \quad [28]$$

Solving the set of Eqs. 21–24, one obtains $-2(\beta_{12}^\lambda - \beta_{14}^\lambda) = 4.74$, $k_1 = 1.305$, $k_2 = 0.56$, and $k_3 = 0.593$ in electron volts (eV; 1 eV = 1.602×10^{-19} J) by taking the values $E(^1E_{1u}) = 6.76$, $E(^1B_{1u}) = 5.96$, $E(^1B_{2u}) = 4.71$, and $E(^3B_{1u}) = 3.59$ eV (4).

From Eq. 19 we obtained $\beta_{12}^\lambda = -2.50$, $\beta_{14}^\lambda = -0.136$, and $-2(\beta_{12}^\lambda - \beta_{14}^\lambda) = 4.73$. Then, we have $\gamma_{11}^\lambda = k_0 + 4.3875$, $\gamma_{12}^\lambda = k_0 + 0.1525$, $\gamma_{13}^\lambda = k_0 - 1.2725$, and $\gamma_{14}^\lambda = k_0 - 2.0825$. By using Eq. 20 we obtain the repulsion integral for the nonorthogonal basis set as $\gamma_{11} = k + 6.1818$, $\gamma_{12} = k + 2.2326$, $\gamma_{13} = k + 0.8344$, $\gamma_{14} = k + 0.0573$, and $k = k_0 - 2.0825$. Setting γ_{11} equal to $I - A$, one then obtains $\gamma_{11} = 10.8$, $\gamma_{12} = 6.935$, $\gamma_{13} = 5.452$, and $\gamma_{14} = 4.676$ eV when I and A were taken to be 11.16 and 0.36, respectively (19).

To reproduce the values for the repulsion integrals, we use a modified form of the Mataga–Nishimoto formula (27, 28)

$$\gamma_{\mu\nu} = \frac{14.397}{\frac{28.784}{\gamma_{\mu\mu} + \gamma_{\nu\nu}} + R_{\mu\nu}^\tau}, \quad [29]$$

Table 1. Comparison of experimental and calculated energy values

Benzene			Cyclopentadienide anion		
State	Value, eV		State	Value, eV	
	Exp.	Calc.		Exp.	Calc.
$^1E_{1u}$	6.75	6.76	1E_2	5.64*	5.64
$^1B_{1u}$	5.96	5.96		5.69†	
$^1B_{2u}$	4.70	4.70		5.96‡	
$^3B_{1u}$	3.59	3.59	E_1^1	—	6.71
$-2(\beta_{12}^1 - \beta_{14}^1)$	4.73	4.74	$-2.236(\beta_{12}^1 - \beta_{13}^1)$	—	4.75

$\tau = 1 + aR_{\mu\nu} + bR_{\mu\nu}^2$, $a = -0.536$, $b = 0.144$. Exp., experimental value; Calc., calculated value.

* Cation = K^+ .

† Cation = Na^+ .

‡ Cation = Li^+ .

where $\tau = 1 + aR_{\mu\nu} + bR_{\mu\nu}^2$, with $a = -0.536$ and $b = 0.144$. By using Eqs. 19 and 29, one obtains almost exact energy values for the benzene molecule, including the $^3B_{1u}$ state.

For the cyclopentadienide anion, one obtains $a = -0.539$ and $b = 0.151$ for the τ in the repulsion integral formula by a procedure analogous to that for the benzene molecule. The two sets of parameters for the cyclopentadienide anion and benzene are almost identical. Evidently, we can take the parameters for the benzene molecule as fixed values for the π system (e.g., cyclopentadienide anion, benzene). It will be useful to know how general this result is.

The energy values calculated by using the parameters for the cyclopentadienide anion for benzene are the same as those found experimentally (29–31). The results are shown in Table 1.

Discussion

The use of the formula for the resonance integrals for the non-orthogonal basis set in the polyatomic approach depends on the choice of the basis set because of the overlap integrals. But the uncertainty becomes smaller because of the symmetrical orthogonalization. In computing the quantity $\beta_{\mu\nu}$ in Eq. 18, we adopted the Linderberg method (22) as

$$\beta_{\mu\nu} = \frac{\hbar^2}{mR_{\mu\nu}} \frac{\partial S_{\mu\nu}}{\partial R_{\mu\nu}}.$$

At present, the parameters for the repulsion integrals are used to best fit the experimental results in the Mataga–Nishimoto formula. However, the use of a formula that does not have any parameters to be adjusted would be desirable.

In the Berthier (11) resonance integral, the $\epsilon_{\mu\nu}$ of Eq. 19 is introduced to avoid a vanishing resonance integral for the orthogonal basis set. $\epsilon_{\mu\nu}$ of Eq. 19 is naturally introduced from

the Heisenberg equation of motion and the modified Dirac (26) resolution of identity, Eq. 11. Also, the formula derived here has a proper limit when the two centers, μ and ν , are superimposed.

As seen from Eq. 15, the formula gives an interpretation of the parameter κ for the semiempirical resonance integrals originated in the Mulliken approximation.

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- Seitz, F. (1940) *The Modern Theory of Solids* (McGraw-Hill, New York), pp. 335–339.
- Pariser, R. & Parr, R. G. (1953) *J. Chem. Phys.* **21**, 466–471.
- Pariser, R. & Parr, R. G. (1953) *J. Chem. Phys.* **21**, 767–776.
- Pariser, R. (1953) *J. Chem. Phys.* **21**, 568–569.
- Parr, R. G. (1959) *J. Chem. Phys.* **24**, 250–268.
- Pariser, R. (1959) *J. Chem. Phys.* **25**, 1112–1116.
- Pople, J. A. (1953) *Trans. Faraday Soc.* **49**, 1397–1399.
- Löwdin, P.-O. (1955) *Phys. Rev.* **97**, 1490–1508.
- Gladney, H. M. (1963) *Theor. Chim. Acta* **1**, 245–256.
- Fischer-Hjalmars, I. (1965) in *Advances in Quantum Chemistry*, ed. Löwdin, P.-O. (Academic, New York), Vol. 2, pp. 25–27.
- Berthier, G., Banvet, J. & Suard, M. (1963) *Tetrahedron Suppl.* **2**, 19, 1–14.
- Koutecký, J. (1967) *Chem. Phys. Lett.* **1**, 249–250.
- Linderberg, J. & Öhrn, Y. (1965) *Proc. R. Soc. London Ser. A* **285**, 445–456.
- Nishimoto, K. & Forster, L. S. (1965) *Theor. Chim. Acta* **4**, 155–165.
- Fischer-Hjalmars, I. (1966) *Theor. Chim. Acta* **4**, 332–342.
- Fischer-Hjalmars, I. (1962) *Ark. Fys.* **21**, 123–143.
- Fischer-Hjalmars, I. (1964) in *Molecular Orbitals in Chemistry, Physics and Biology*, eds. Löwdin, P.-O. & Pullman, B. (Academic, New York), pp. 361–365.
- Fischer-Hjalmars, I. (1965) *J. Chem. Phys.* **42**, 1962–1972.
- Adams, O. W. & Miller, R. L. (1966) *J. Am. Chem. Soc.* **88**, 404–412.
- Adams, O. W. & Miller, R. L. (1968) *Theor. Chim. Acta* **12**, 151–165.
- Linderberg, J. (1967) *Chem. Phys. Lett.* **1**, 39–41.
- Linderberg, J. & Seamans, L. (1972) *Mol. Phys.* **24**, 1393–1405.
- Mulliken, R. S. (1949) *J. Chim. Phys.* **46**, 497–542.
- Goepfert-Mayer, M. & Sklar, A. L. (1938) *J. Chem. Phys.* **6**, 645–652.
- Schiff, L. I. (1968) *Quantum Mechanics* (McGraw-Hill, New York), 2nd Ed., pp. 307–309.
- Dirac, P. A. M. (1958) *Quantum Mechanics* (Oxford Univ. Press, Fair Lawn, NJ).
- Nishimoto, K. & Mataga, M. (1957) *Z. Phys. Chem. (Frankfurt am Main)* **12**, 335–338.
- Nishimoto, K. & Mataga, M. (1957) *Z. Phys. Chem. (Frankfurt am Main)* **13**, 140–144.
- Ford, W. T. (1971) *J. Organomet. Chem.* **32**, 27–33.
- Wagner, B. O. & Ebel, H. (1970) *Tetrahedron* **26**, 5155–5167.
- Klevens, H. B. & Platt, J. R. (1949) *J. Chem. Phys.* **17**, 470–481.