Theoret. chim. Acta (Berl.) 4, 250—259 (1966)

Department of Mathematics, University of Nottingham, Nottingham, England

Relativistic Effects in Aromatic Molecules

Orbit-Orbit Coupling in the Presence of a Magnetic Field Evaluation of Integrals Involving the Interelectronic Coordinate*

By

Ralph E. Christoffersen** and **G. G. Hall**

Evaluation of the relativistic correction due to the orbit-orbit operator of the Breit Hamiltonian has been considered in general, including the presence of a magnetic field. For conjugated molecules, the change in energy due to this relativistic effect is shown to be expressible in terms of two types of integrals and their derivatives. The interaction results in an intermolecular contribution to the diamagnetic susceptibility which, for two parallel benzene rings, is found to be smaller than the molecular terms by a factor of α^2. Several molecular integrals not previously evaluated were encountered, and their evaluation as asymptotic expansions is discussed.

Die Berechnung eines relativistischen Termes, nämlich des Bahn-Bahn-Anteiles des Breit'schen Hamilton-Operators, ist bei vorhandenem Magnetfeld in allgemeiner Form durchgeführt worden. Bei konjugierten Molekülen erscheinen im Ausdruck für die zugehörige Energieänderung zwei Arten von Integralen und ihren Ableitungen. Die Wechselwirkung liefert einen intermolekularen Beitrag zur diamagnetischen Suszeptibilität, der allerdings im Fall zweier paralleler Benzolringe um den Faktor α^2 kleiner als die innermolekularen Terme ist. In diesem Zusammenhang traten einige bisher nicht benötigte Integrale auf, deren asymptotische Entwicklung durchgeführt wurde.

Nous avons étudié, en forme générale, la correction relativiste due a l'operateur orbite-orbite de Breit en présence d'un champ magnétique. Pour les molécules conjuguées, l'effet énergétique de ce terme peut être exprimé par deux types d'intégrales et leurs dérivées. La contribution intermoléculaire a la susceptibilité diamagnetique est trouvée, pour deux noyaux parallèles de benzène, d'être d'un facteur α^2 plus petit que les termes moléculaires. Quelques intégrales moléculaires, incalculées jusque la, ont été évaluées par expansion asymptotique.

I. Introduction

It is now well known that the study of relativistic corrections, although often small in magnitude for systems with low nuclear charges, can offer much new insight into physical and chemical processes. Although some operators corresponding to relativistic effects have been studied in great detail, such as spin-orbit and spin-spin operators, there has been no general treatment for another operator of this type, namely the orbit-orbit operator. This paper gives a general treatment of matrix elements over this operator, including the presence of a

---

* This investigation was supported in part by Public Health Service Fellowship No. 1F2 GM-18, 898-01 from the Division of General Medical Sciences, National Institutes of Health, U.S.A.

** Present Address: Department of Chemistry, Iowa State University, Ames, Iowa 50010. Address after September 1, 1966: Department of Chemistry, University of Kansas, Lawrence, Kansas 66045.

magnetic field, and employs mathematical techniques that may be quite useful in treating other operators of a similar type. Also, this paper considers how the presence of the magnetic field and orbit-orbit interaction may affect the quantum mechanical theories [*4, 6, 3*] concerning diamagnetic susceptibility.

Within a crystal, one of the ways in which the molecules may interact is via the magnetic field. In particular, the orbital angular momentum of an electron in one aromatic ring may produce a magnetic field which interacts with the orbital angular momentum of another electron in a neighboring ring. The next section deals directly with the nature of this effect, by treating the general evaluation of matrix elements of the orbit-orbit operator, with special reference to the manner in which wavefunctions should be chosen when magnetic fields are present. The third section deals with the specific case of two parallel benzene rings, where the geometry suggests that the effect might be significant. There are also other effects from neighbors which are of the same order of magnitude, and a discussion of these, as well as the orbit-orbit effect, appears in section four. Finally, during the course of this work, some integrals involving the interelectronic coordinate arose that have not been evaluated previously, and the method of evaluation and error analysis are included in the Appendix.

II. General Treatment of Matrix Elements

The interaction of the orbital angular momenta of electrons was considered first by BREIT [*1*], in a relativistic treatment of the Schroedinger equation. When generalized to N electrons, the orbit-orbit Hamiltonian in atomic units [*10*] is

$$\mathscr{H} = -\tfrac{1}{2}\,\alpha^2 \sum_{j<k}^{N} \left[\frac{\boldsymbol{p}_j \cdot \boldsymbol{p}_k}{r_{jk}} + \frac{\boldsymbol{r}_{jk} \cdot (\boldsymbol{r}_{jk} \cdot \boldsymbol{p}_j)\, \boldsymbol{p}_k}{r_{jk}^3} \right], \tag{1}$$

in which $\boldsymbol{p}_j$ is the momentum of the jth electron, α is the fine structure constant and r_{jk} is the scalar interelectronic distance. In later use, the subscripts j and k will refer to electrons in different molecules, each molecule containing $N/2$ electrons.

In the presence of an external magnetic field, the momentum becomes dependent upon the vector potential, *i. e.*, $\boldsymbol{p}_j = \boldsymbol{p}_j^0 + \alpha \boldsymbol{A}_j = 1/i\,(\nabla_j + i\alpha \boldsymbol{A}_j)$, where atomic units are used. Thus, (1) can be rewritten as

$$\begin{aligned}\mathscr{H} = \left(\frac{\alpha^2}{2}\right) \sum_{j<k}^{N} \Bigg\{ & \frac{1}{r_{jk}} \left[\nabla_j \cdot \nabla_k + i\alpha\, (\boldsymbol{A}_j \cdot \nabla_k + \nabla_j \cdot \boldsymbol{A}_k) - \alpha^2\, \boldsymbol{A}_j \cdot \boldsymbol{A}_k\right] + \\ & + \frac{1}{r_{jk}^3} [\boldsymbol{r}_{jk} \cdot (\boldsymbol{r}_{jk} \cdot \nabla_j)\, \nabla_k + i\alpha\, (\boldsymbol{r}_{jk} \cdot (\boldsymbol{r}_{jk} \cdot \nabla_j)\, \boldsymbol{A}_k + \\ & + \boldsymbol{r}_{jk} \cdot (\boldsymbol{r}_{jk} \cdot \nabla_k)\, \boldsymbol{A}_j) - \alpha^2\, (\boldsymbol{r}_{jk} \cdot (\boldsymbol{r}_{jk} \cdot \boldsymbol{A}_j)\, \boldsymbol{A}_k)] \Bigg\}, \end{aligned} \tag{2}$$

where $\boldsymbol{A}_j$ is the vector potential of the jth electron. If the magnetic field $\boldsymbol{H}$ is uniform, then $\boldsymbol{A} = \tfrac{1}{2}\,(\boldsymbol{H} \times \boldsymbol{r})$, where the origin of $\boldsymbol{r}$ is arbitrary, so that the kinetic energy depends upon the choice of origin, and is not the same around equivalent nuclei. This can be avoided by the use of basis orbitals which contain a phase factor. The proper choice of this phase factor has been shown [*3*] to be

$$\omega_\beta\,(j) = \varphi_\beta\,(j)\, e^{-i\alpha\, \boldsymbol{A}_{\beta j} \cdot \boldsymbol{r}_j}, \tag{3}$$

where $\boldsymbol{A}_{\beta j}$ is the vector potential measured from nucleus β, and $\varphi_\beta\,(j)$ is an atomic orbital*, independent of $\boldsymbol{A}_{\beta j}$. By the use of (3), we see that

$$(\nabla_j + i\alpha\,\boldsymbol{A}_j)\,\omega_\beta\,(j) = e^{-i\alpha\,\boldsymbol{A}_{\beta j}\cdot\boldsymbol{r}_j}\,[\nabla_j + i\alpha\,(\boldsymbol{A}_j - \boldsymbol{A}_{\beta j})]\,\varphi_\beta\,(j)\,. \tag{4}$$

We now consider the general matrix element, $H_{\beta\gamma\delta\varepsilon}$, over orbitals of the type ω_β, *i. e.*,

$$\begin{aligned} H_{\beta\gamma\delta\varepsilon} = \int\int \exp\,\{i\alpha\,[(\boldsymbol{A}_{\beta j} - \boldsymbol{A}_{\delta j})\cdot\boldsymbol{r}_j + (\boldsymbol{A}_{\gamma k} - \boldsymbol{A}_{\varepsilon k})\cdot\boldsymbol{r}_k]\}& \\ \varphi_\beta^*\,(j)\,\varphi_\gamma^*\,(k)\,\mathscr{H}\,(j,k)\,\varphi_\delta\,(j)\,\varphi_\varepsilon\,(k)\,d\tau_{j,\,k}\,.& \end{aligned} \tag{5}$$

Next, the Pariser-Parr approximation of "zero differential overlap" [7] is employed, *i. e.*, these elements vanish except when $\beta = \delta$ and $\gamma = \varepsilon$. When this is used in conjunction with (4), we obtain

$$\begin{aligned} H_{\beta\gamma\beta\gamma} = \left(\frac{\alpha^2}{2}\right)\int\int \varphi_\beta^*\,(j)\,\varphi_\gamma^*\,(k)\,\Big\{\frac{1}{r_{jk}}\,&[\nabla_j\cdot\nabla_k + i\alpha\,((\boldsymbol{A}_j - \boldsymbol{A}_{\beta j})\cdot\nabla_k + \\ &+ \nabla_j\cdot(\boldsymbol{A}_k - \boldsymbol{A}_{\gamma k})) - \alpha^2\,(\boldsymbol{A}_j - \boldsymbol{A}_{\beta j})\cdot(\boldsymbol{A}_k - \boldsymbol{A}_{\gamma k})] + \\ &+ [\boldsymbol{r}_{jk}\cdot(\boldsymbol{r}_{jk}\cdot\nabla_j)\,\nabla_k + i\alpha\,(\boldsymbol{r}_{jk}\cdot(\boldsymbol{r}_{jk}\cdot\nabla_j)\,(\boldsymbol{A}_k - \boldsymbol{A}_{\gamma k}) + \\ &+ \boldsymbol{r}_{jk}\cdot(\boldsymbol{r}_{jk}\cdot\nabla_k)\,(\boldsymbol{A}_j - \boldsymbol{A}_{\beta j})) - \\ &- \frac{\alpha^2}{r_{jk}^3}\,(\boldsymbol{r}_{jk}\cdot[\boldsymbol{r}_{jk}\cdot(\boldsymbol{A}_j - \boldsymbol{A}_{\beta j})]\,[\boldsymbol{A}_k - \boldsymbol{A}_{\gamma k}])]\Big\}\,\varphi_\beta\,(j)\,\varphi_\gamma\,(k)\,d\tau_{j,\,k}\,. \end{aligned} \tag{6}$$

First we treat the terms in r_{jk}^{-1}, which are usually called the non-retardation terms. It can be shown that, for ordinary diamagnetic substances like benzene, the coefficients of the integrals involving the terms linear in the field vanish**. Then, by using the general property that

$$\nabla_j\,\varphi_\beta\,(j) = -\nabla_\beta\,\varphi_\beta\,(j)\,, \tag{7}$$

and also noting that $\boldsymbol{r}_{\beta j} = \boldsymbol{r}_j - \boldsymbol{R}_\beta$, which means that $\boldsymbol{A}_j - \boldsymbol{A}_{\beta j} = \frac{1}{2}\,(\boldsymbol{H}\times\boldsymbol{R}_\beta)$, we may write the contribution of the non-retarded portion as

$$H_{\mathrm{NR}} = \frac{\alpha^2}{8}\,\{\nabla_\beta\cdot\nabla_\gamma - \alpha^2\,H_z^2\,(X_\beta\,X_\gamma + Y_\beta\,Y_\gamma)\}\iint \varphi_\beta^*\,(j)\,\varphi_\gamma^*\,(k)\,\frac{1}{r_{jk}}\,\varphi_\beta\,(j)\,\varphi_\gamma\,(k)\,d\tau_{j,\,k}\,, \tag{8}$$

where $\boldsymbol{R}_\beta$ has components $(X_\beta,\ Y_\beta,\ Z_\beta)$ and we have assumed that the magnetic field is directed along the z axis. We note that, in order to evaluate the non-retardation terms, it is only necessary to be able to calculate the ordinary coulomb electron repulsion integral.

Next, we consider the retardation terms. As before, the coefficients of the terms linear in the field will vanish for ordinary diamagnetic substances such as benzene, and only four terms remain to be considered. By using (7), the two terms independent of the field, $H_{\mathrm{R}}^{(\mathrm{FI})}$, can be written as

$$H_{\mathrm{R}}^{(\mathrm{FI})} = \left(\frac{\alpha^2}{4}\right)\nabla_\beta\cdot\int\int \varphi_\beta^*\,(j)\,\varphi_\gamma^*\,(k)\,\frac{\boldsymbol{r}_{jk}}{r_{jk}^3}\,(\nabla_\gamma\cdot\boldsymbol{r}_{jk})\,\varphi_\beta\,(j)\,\varphi_\gamma\,(k)\,d\tau_{j,\,k}\,. \tag{9}$$

---

* Throughout this paper, greek subscripts will be used to refer to nuclei, and italic subscripts will be used to refer to electrons.

** The proof of this for molecules with doubly occupied orbitals can be seen by an examination of equation (5.07) in reference [*3*].

We now note that $\nabla_j\,(1/r_{jk}) = -\,\boldsymbol{r}_{jk}/r_{jk}^3$, and also that

$$\nabla_j\,[\varphi_\beta\,(j)/r_{jk}] = \varphi_\beta\,(j)\,\nabla_j\,(1/r_{jk}) + (1/r_{jk})\,\nabla_j\,\varphi_\beta\,(j)\,, \tag{10}$$

which allows (9) to be rewritten as

$$H_{\mathrm{R}}^{(\mathrm{FI})} = -\,\frac{\alpha^2\,\nabla_\beta{}^2}{16}\,\nabla_\gamma\cdot\iint \varphi_\beta^*\,(j)\,\varphi_\gamma^*\,(k)\,\frac{\boldsymbol{r}_{jk}}{r_{jk}}\;\varphi_\beta\,(j)\,\varphi_\gamma\,(k)\,d\tau_{j,\,k}\,, \tag{11}$$

where the term on the left of (10) has been omitted, since it can be transformed to a surface integral which vanishes as the surface gets large. Finally, we use the relation $\nabla_k\,(r_{jk}) = -\,\boldsymbol{r}_{jk}/r_{jk}$ to rewrite (11) eventually as

$$H_{\mathrm{R}}^{(\mathrm{FI})} = +\,(\alpha^2\,\nabla_\beta^2\,\nabla_\gamma^2/32)\iint \varphi_\beta^*\,(j)\,\varphi_\gamma^*\,(k)\,r_{jk}\,\varphi_\beta\,(j)\,\varphi_\gamma\,(k)\,d\tau_{j,\,k}\,. \tag{12}$$

By entirely similar procedures the remaining two terms of the retardation portion can be evaluated, and the general matrix element written as the sum of H_{NR} and H_{R}, *i. e.*,

$$\begin{aligned} H_{\beta\gamma\beta\gamma} = \frac{\alpha^2}{8}\{\,&[\nabla_\beta\cdot\nabla_\gamma - \alpha^2\,H_{\mathrm{z}}^2\,(X_\beta\,X_\gamma + Y_\beta\,Y_\gamma)]\iint \varphi_\beta^*\,(j)\,\varphi_\gamma^*\,(k)\,\frac{1}{r_{jk}}\,\varphi_\beta\,(j)\,\varphi_\gamma\,(k)\,d\tau_{j,\,k} + \\ &+ \tfrac{1}{4}\,[\nabla_\beta^2\,\nabla_\gamma^2 - \alpha^2\,(\boldsymbol{B}\cdot\nabla_\beta)\,(\boldsymbol{C}\cdot\nabla_\gamma)]\iint \varphi_\beta^*\,(j)\,\varphi_\gamma^*\,(k)\,r_{jk}\,\varphi_\beta\,(j)\,\varphi_\gamma\,(k)\,d\tau_{j,\,k}\}\,, \end{aligned} \tag{13}$$

where $\boldsymbol{B} = \boldsymbol{H}\times\,\boldsymbol{R}_\beta$, and $\boldsymbol{C} = \boldsymbol{H}\times\,\boldsymbol{R}_\gamma$.

There are several things to be noted about the above result. First of all, the only approximation that has been made was that of the Pariser-Parr approximation. Secondly, by transforming the operators before performing the integrations, instead of attempting to evaluate integrals over complicated operators, a final expression was obtained which contains only two integrals. The first of these is the well known electron repulsion integral, which is met in molecular calculations of almost any kind, and the methods of evaluating it are well known [*9*]. The integral which appears in the retardation term is not as well known, and the techniques for its evaluation have only been given for the simplest case, namely when all the orbitals are 1*s* orbitals [*2*].

III. Application to Two Parallel Benzene Rings

We shall now confine our attention to the special case of the twelve π electrons involved in two parallel benzene rings. It is desired to calculate the perturbation energy, given by

$$E = \sum_{j=1}^{6}\,\sum_{k=7}^{12}\int\cdots\int \Psi^*\,(1, 2, \ldots, 12)\,\mathscr{H}\,(j, k)\,\Psi\,(1, 2, \ldots, 12)\,d\tau_{1\,\ldots,\,12}. \tag{14}$$

It will be assumed that the total wave function Ψ can be written as the product $\Psi_1\,(1, 2, \ldots, 6)\,\Psi_2\,(7, 8, \ldots, 12)$, where the first six electrons are all in the same ring, and similarly for the last six electrons. This corresponds to the physical assumption that there is no exchange between electrons in different rings. A single, normalized Slater determinant will be used for Ψ_1 (similarly for Ψ_2), *i. e.*,

$$\Psi_1 = (6\,!)^{-\frac{1}{2}}\det\{\Phi_0\,(1)\,\overline{\Phi}_0\,(2)\,\Phi_1\,(3)\,\overline{\Phi}_1\,(4)\,\Phi_{-1}\,(5)\,\overline{\Phi}_{-1}\,(6)\}\,, \tag{15}$$

in which Φ_0, Φ_1 and Φ_{-1} are orthonormal molecular orbitals and Φ_μ and $\overline{\Phi}_\mu$ are orthogonal due to the choice of spin factor. In particular, the λ_μ, which are the spatial parts of Φ_μ and $\overline{\Phi}_\mu$, are chosen from the set of orthonormal orbitals

$$\lambda_\mu = \frac{1}{\sqrt{6}}\sum_{\beta=1}^{6}\exp\left\{\frac{i\mu\beta\pi}{3}\right\}\omega_\beta\,. \qquad (\mu = 0,\ \pm 1,\ \pm 2)\,. \tag{16}$$

The ω_β are the field-dependent orbitals given in (3), and the φ_β have been chosen to be the ordinary Slater-type $2p_z$ orbitals. Strictly speaking, orbitals orthogonalized by the Löwdin scheme [5] would be the proper choice for the φ_β, but for the large internuclear distances that were encountered here, the use of non-orthogonalized orbitals gives essentially equivalent results.

We may now write (14) as

$$\begin{aligned} E = (6!)^{-2} \sum_{j=1}^{6} \sum_{k=7}^{12} \int \ldots \int \det \{ & \Phi_{01}^{*}(1)\, \bar{\Phi}_{01}^{*}(2)\, \Phi_{11}^{*}(3)\, \bar{\Phi}_{11}^{*}(4)\, \Phi_{-11}^{*}(5) \bar{\Phi}_{-11}^{*}(6)\} \\ & . \det \{\Phi_{02}^{*}(7)\, \bar{\Phi}_{02}^{*}(8)\, \Phi_{12}^{*}(9)\, \bar{\Phi}_{12}^{*}(10)\, \Phi_{-12}^{*}(11)\, \bar{\Phi}_{-12}^{*}(12)\}\, \mathscr{H}(j,k) \\ & . \det \{\Phi_{01}(1)\, \bar{\Phi}_{01}(2)\, \Phi_{11}(3) \bar{\Phi}_{11}(4)\, \Phi_{-11}(5)\, \bar{\Phi}_{-11}(6)\} \\ & . \det \{\Phi_{02}(7)\, \bar{\Phi}_{02}(8)\, \Phi_{12}(9)\, \bar{\Phi}_{12}(10)\, \Phi_{-12}(11)\, \bar{\Phi}_{-12}(12)\}\, d\tau_{1,\ldots,12}, \end{aligned} \tag{17}$$

where the second subscript of Φ refers to the ring number. If we now expand the determinants in (17), it can easily be shown that the only non-zero terms have the form

$$J_{\beta,\gamma} = \iint \lambda_{\beta 1}^{*}(j)\, \lambda_{\gamma 2}^{*}(k)\, \mathscr{H}(j,k)\, \lambda_{\beta 1}(j)\, \lambda_{\gamma 2}(k)\, d\tau_{j,k}\,. \tag{18}$$

Note that none of the exchange integrals that usually arise in molecular calculations are present, and this is due to the assumption that there is no exchange of electrons between rings. In particular, the only non-zero contributions to E are given by

$$E = 4\,[J_{0,0} + J_{0,1} + J_{0,-1} + J_{1,0} + J_{1,-1} + J_{-1,0} + J_{-1,+1} + J_{-1,-1} + J_{1,1}]\,. \tag{19}$$

When the "zero differential overlap" concept is applied to the elements of (19), we obtain the simple result

$$E = \sum_{\beta,\gamma=1}^{6} \iint \varphi_{\beta 1}^{*}(1)\, \varphi_{\gamma 2}^{*}(7)\, \mathscr{H}(1,7)\, \varphi_{\beta 1}(1)\, \varphi_{\gamma 2}(7)\, d\tau_{1,} = \sum_{\beta,\gamma=1}^{6} C_{\beta\gamma}\,. \tag{20}$$

By noting further that all of the diagonal terms in (20) give the same result, and that $C_{ij} = C_{ji}$, and $C_{12} = C_{23} = C_{34}$, $C_{13} = C_{24} = C_{35}$, ..., etc., we obtain

$$E = 6\,[C_{11} + C_{14} + 2\,(C_{12} + C_{13})]\,. \tag{21}$$

For the evaluation of the terms in (21), the origin has been chosen to be halfway between the centers of the two rings, and the orientation of the x, y, z axes is shown in Fig. 1.

Next, we consider C_{11}. If we use $R_{\mathrm{C-C}} = 2.6266$ Bohrs (= 1.390 Å) as the carbon-carbon distance between neighbors in a ring, then

$$\boldsymbol{B}\cdot\nabla_{11} = X_{11}\, H_z\, \boldsymbol{j}\cdot\nabla_{11} = -\,2.6266\, H_z \frac{\partial D_{11}}{\partial Y_{11}} \cdot \frac{\partial}{\partial D_{11}}\,.$$

But, $D_{11} = [(X_{12} - X_{11})^2 + (Y_{12} - Y_{11})^2 + (Z_{12} - Z_{11})^2]^{\frac{1}{2}}$, and so

$$\frac{\partial D_{11}}{\partial Y_{11}} = -\,\frac{(Y_{12} - Y_{11})}{D_{11}} = 0\,.$$

Thus

$$\begin{aligned} C_{11} = \frac{\alpha^2}{8} \{ & [\nabla_{11}\cdot\nabla_{12} - 6.89903\cdot\alpha^2 H_z^2]\, \gamma\,(D_{11}; 2p_z, 2p_z) + \\ & + \tfrac{1}{4}\, \nabla_{11}^2\, \nabla_{12}^2\, \delta\,(D_{11}; 2p_z, 2p_z)\}\,, \end{aligned} \tag{22}$$

where the two basic integrals are defined as

$$\gamma\,(D_{\alpha\beta};\,\varphi_{\alpha 1},\varphi_{\beta 2}) = \iint \varphi_{\alpha 1}^{*}(1)\,\varphi_{\beta 2}^{*}(7)\,\frac{1}{r_{17}}\,\varphi_{\alpha 1}(1)\,\varphi_{\beta 2}(7)\,d\tau_{1,7}\ ,$$

$$\delta\,(D_{\alpha\beta};\,\varphi_{\alpha 1},\varphi_{\beta 2}) = \iint \varphi_{\alpha 1}^{*}(1)\,\varphi_{\beta 2}^{*}(7)\,r_{17}\,\varphi_{\alpha 1}(1)\,\varphi_{\beta 2}(7)\,d\tau_{1,7}\,. \tag{23}$$

Similarly for C_{14}, we see that

$$C_{14} = \frac{\alpha^2}{8}\,[(\nabla_{11}\cdot\nabla_{42} + 6.89903\cdot\alpha^2 H_z^2)\,\gamma\,(D_{14}) + \tfrac{1}{4}\,\nabla_{11}^2\,\nabla_{42}^2\,\delta\,(D_{14})]\,, \tag{24}$$

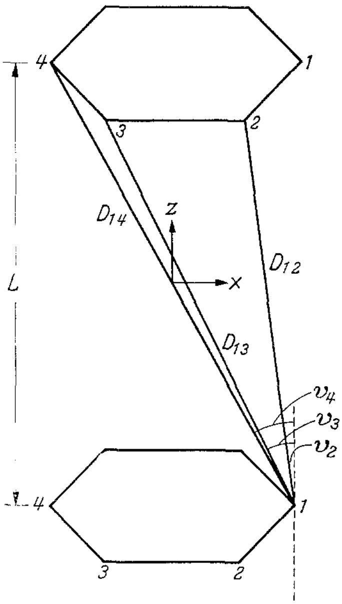

Fig. 1. The coordinate system chosen for the case of two parallel benzene rings. The y-axis points out of the paper

where $\gamma\,(D_{14})$ and $\delta\,(D_{14})$ are abbreviations for the integrals in (23). However, the orbitals must be expressed as linear combinations of their components, *e. g.*,

$$\gamma\,(D_{14}) = \cos^4\theta_4\cdot\gamma\,(D_{14};\,2p_z,2p_z) + 2\sin^2\theta_4\cos^2\theta_1\cdot\gamma\,(D_{14};\,2p_z,2p_x) + \\ + \sin^4\theta_1\cdot\gamma\,(D_{14};\,2p_x,2p_x)\,, \tag{25}$$

where the contribution from non-Coulombic integrals has been neglected. The proof that this term can be omitted is given in the Appendix.

In a similar manner, the contribution from C_{12} and C_{13} can be evaluated, giving

$$C_{12} = \frac{\alpha^2}{8}\,[(\nabla_{11}\cdot\nabla_{22} - 3.44951\,\alpha^2 H_z^2)\,\gamma\,(D_{12}) + \\ + \tfrac{1}{4}\left(\nabla_{11}^2\,\nabla_{22}^2 + 35.69744\,\frac{\alpha^2 H_z^2}{D_{12}^2}\cdot\frac{\partial^2}{\partial D_{12}^2}\right)\delta\,(D_{12})]\ , \tag{26}$$

$$C_{13} = \frac{\alpha^2}{8}\,[(\nabla_{11}\cdot\nabla_{32} + 3.44951\,\alpha^2 H_z^2)\,\gamma\,(D_{13}) + \\ + \tfrac{1}{4}\left(\nabla_{11}^2\,\nabla_{32}^2 + 35.69744\,\frac{\alpha^2 H^2}{D_{13}^2}\cdot\frac{\partial^2}{\partial D_{13}^2}\right)\delta\,(D_{13})]\,.$$

By substituting the results of (22), (24) and (26) into (21), we can then separate the terms into two types, those independent of the magnetic field, and those dependent on H_z^2. The effect on the diamagnetic susceptibility is then obtained as the second derivative of E with respect to H_z, *i. e.*,

$$\frac{\partial^2 E}{\partial H_z^2} = \frac{3\,\alpha^4 f}{2}\ , \tag{27}$$

where

$$f = (6.89903)\cdot[\gamma\,(D_{14}) + \gamma\,(D_{13}) - \gamma\,(D_{11}) - \gamma\,(D_{12})] + \\ + 17.84872\ \cdot \left[\frac{1}{D_{13}^2}\,\frac{\partial^2}{\partial D_{13}^2}\,\delta\,(D_{13}) + \frac{1}{D_{12}^2}\,\frac{\partial^2}{\partial D_{12}^2}\,\delta\,(D_{12})\right]. \tag{28}$$

If we then choose $L = 4.811$ Bohrs as the distance between the rings, and 3.18 as the orbital exponent of the Slater-type $2p_z$ (and $2p_x$) orbitals, we then obtain the result

$$\chi = -\frac{\partial^2 E}{\partial H_z^2} = +\,7.0 \times 10^{-5}\,\alpha^2\,. \tag{29}$$

IV. Discussion

From previous work done on benzene in the absence of orbit-orbit coupling, it can be seen that, for two isolated benzene rings, the diamagnetic susceptibility is given by $\chi = -\,25.14\,\alpha^2$ [*3*]. Therefore, the orbit-orbit effect on the susceptibility due to a parallel nearest neighbor is very small and paramagnetic, and thus will tend to decrease the total measured diamagnetic susceptibility only slightly.

It is interesting to aks if there is a possible classical analog to the orbit-orbit effect calculated here. The classical effect which comes closest to this is the change in energy of two parallel rings carrying currents in a magnetic field due to their mutual inductance. However, the only way of obtaining a non-zero result for the energy is either to allow the rings to move, or to vary the magnetic field. But, both of these possibilities are denied in the quantum mechanical calculations done here. Thus, it seems that there is no classical analog, and that the orbit-orbit coupling effect discussed here is strictly a quantum effect.

It should also be noted that the effect calculated here is certainly not the only effect of the order of magnitude of α^2 that can be considered. For example, there are contributions due to the quantum mechanical analogs of the classical effects mentioned previously, which could be considered either by applying an oscillating field to the molecules fixed in space, or by allowing the molecules to vibrate in a constant magnetic field.

Since it has been found here that the orbit-orbit term does not give a significant contribution to the diamagnetic susceptibility, even under favorable conditions, it seems that further study of the effects of this order of magnitude on the diamagnetic susceptibility is not warranted, for their magnitude will certainly be far below the accuracy with which present day experiments can measure the susceptibility. Thus, it seems that, as far as interactions by means of orbit-orbit coupling (via the magnetic field) is concerned, a consideration of only the isolated molecules should give perfectly adequate results for diamagnetic susceptibilities, since the contribution of the nearest neighbors to the susceptibility has been shown to be smaller than the isolated molecule contribution by a factor of α^2.

However, as a relativistic correction, orbit-orbit coupling may become quite significant for molecules involving very heavy atoms, for the effect will become much more pronounced as the nuclear charge is increased.

Appendix

Integral Evaluation. It can be seen from (23) in the text that two types of integrals arise in this work. The first type has been well studied [*9*], and analytical methods are available for its evaluation for all of the Slater-type orbitals involved here. Since the value of the distance parameter D ($= \zeta R$) in these calculations was 15 or greater, there is no need to employ the analytical methods, but an asymptotic expansion can be expected to yield entirely equivalent results. The asymptotic expansions for most of the γ integrals needed here have been given by PARR [*8*]. The only one not given explicitly in that paper can be easily obtained from the general formula given there, and for completeness, all of the integrals needed for these calculations are given below in atomic units, and α, β refer to the two nuclei.

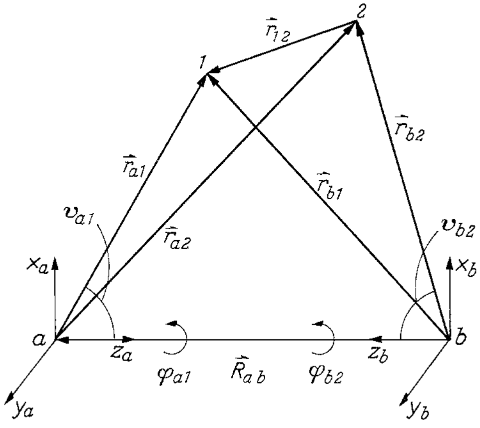

Fig. 2. The coordinate system chosen for the evaluation of the integrals involving the interelectronic coordinate explicitly

$$\int\int 2p_z(\alpha\, 1)\, 2p_z(\beta\, 2) \frac{1}{r_{12}} 2p_z(\alpha\, 1)\, 2p_z(\beta\, 2)\, d\tau_{12} = \zeta\left[\frac{1}{D} + \frac{24}{D^3} + \frac{864}{D^5}\right]$$

$$\int\int 2p_z(\alpha\, 1)\, 2p_x(\beta\, 2) \frac{1}{r_{12}} 2p_z(\alpha\, 1)\, 2p_x(\beta\, 2)\, d\tau_{12} = \zeta\left[\frac{1}{D} + \frac{6}{D^3} - \frac{432}{D^5}\right]$$

$$\int\int 2p_x(\alpha\, 1)\, 2p_x(\beta\, 2) \frac{1}{r_{12}} 2p_x(\alpha\, 1)\, 2p_x(\beta\, 2)\, d\tau_{12} = \zeta\left[\frac{1}{D} - \frac{12}{D^3} + \frac{324}{D^5}\right]. \quad \text{(A-1)}$$

The situation with respect to the δ integrals was much less satisfactory, since the analytical formulae for their evaluation have only been given for all 1*s* orbitals [*2*]. Since these integrals also are necessary ingredients of any calculation in which it is desired to introduce correlation directly into the basis orbitals, it is essential that the correct behavior of these integrals as a function of D is understood. Thus, the following asymptotic expansions were developed for these integrals.

Using the coordinate system shown in Fig. 2, we see that

$$\boldsymbol{r}_{12} = \boldsymbol{r}_{\alpha 1} + \boldsymbol{R}_{\alpha\beta} - \boldsymbol{r}_{\beta 2}\,. \tag{A-2}$$

Thus

$$\begin{aligned} r_{12} &= [\boldsymbol{r}_{12}\cdot\boldsymbol{r}_{12}]^{\frac{1}{2}} = [R_{\alpha\beta}^2 + r_{\alpha 1}^2 + r_{\beta 2}^2 + 2\,\boldsymbol{R}_{\alpha\beta}\cdot\boldsymbol{r}_{\alpha 1} - 2\,\boldsymbol{r}_{\beta 1}\cdot\boldsymbol{r}_{\beta 2}]^{\frac{1}{2}} \\ &= \{1 + (1/R_{\alpha\beta}^2)\,[2\,\boldsymbol{R}_{\alpha\beta}\cdot\boldsymbol{r}_{\alpha 1} - 2\,\boldsymbol{r}_{\beta 1}\cdot\boldsymbol{r}_{\beta 2} + r_{\alpha 1}^2 + r_{\beta 2}^2]\}^{\frac{1}{2}}\,, \end{aligned} \tag{A-3}$$

where the relation $\boldsymbol{r}_{\alpha 1} = \boldsymbol{r}_{\beta 1} - \boldsymbol{R}_{\alpha\beta}$ has been employed. When $R_{\alpha\beta}$ is large, the second term of (A-3) will be much less than 1, and so we may use a binomial expansion to give

$$\begin{aligned} r_{12} = R_{\alpha\beta}\{1 &+ \frac{1}{2\,R_{\alpha\beta}^2}[2\,\boldsymbol{R}_{\alpha\beta}\cdot\boldsymbol{r}_{\alpha 1} - 2\,\boldsymbol{r}_{\beta 1}\cdot\boldsymbol{r}_{\beta 2} + r_{\alpha 1}^2 + r_{\beta 2}^2] - \\ &- \frac{1}{8\,R_{\alpha\beta}^4}[2\,\boldsymbol{R}_{\alpha\beta}\cdot\boldsymbol{r}_{\alpha 1} - 2\,\boldsymbol{r}_{\beta 1}\cdot\boldsymbol{r}_{\beta 2} + r_{\alpha 1}^2 + r_{\beta 2}^2]^2 + \\ &+ \frac{1}{16\,R_{\alpha\beta}^6}[2\,\boldsymbol{R}_{\alpha\beta}\cdot\boldsymbol{r}_{\alpha 1} - 2\,\boldsymbol{r}_{\beta 1}\cdot\boldsymbol{r}_{\beta 2} + r_{\alpha 1}^2 + r_{\beta 2}^2]^3 - \\ &- \frac{5}{128\,R_{\alpha\beta}^8}[2\,\boldsymbol{R}_{\alpha\beta}\cdot\boldsymbol{r}_{\alpha 1} - 2\,\boldsymbol{r}_{\beta 1}\cdot\boldsymbol{r}_{\beta 2} + r_{\alpha 1}^2 + r_{\beta 2}^2]^4 + \ldots\}\,. \end{aligned} \tag{A-4}$$

Using the real, normalized Slater-type orbitals, defined by

$$\varphi\,(n, l, m) = (2\,\zeta)^{n+1/2}\,[(2n)!]^{-1/2}\,r^{n-1}\,e^{-\zeta r}\,S_{l,m}\,(\theta, \varphi)\,, \tag{A-5}$$

where $S_{l,\,m}\,(\theta, \varphi)$ is a real, normalized spherical harmonic, the contributions from the various terms of (A-4) can be evaluated, using either spherical polar or elliptical coordinates to perform the integration. When all of the terms up to and including the term in $R_{\alpha\beta}^{-8}$ are included from (A-4), we obtain the following results for the various integrals needed in these calculations.

$$\begin{aligned} &\iint 2p_z\,(\alpha\,1)\,2p_z\,(\beta\,2)\,r_{12}\,2p_z\,(\alpha\,1)\,2p_z\,(\beta\,2)\,d\tau_{1,2} \\ &= R_{\alpha\beta}\left\{1 + \frac{3}{D^2} - \frac{159}{4\,D^4} - \frac{11{,}853}{2\,D^6} - \frac{5{,}111{,}505}{128\,D^8}\right\}, \end{aligned} \tag{A-6}$$

$$\begin{aligned} &\iint 2p_x\,(\alpha\,1)\,2p_x\,(\beta\,2)\,r_{12}\,2p_x\,(\alpha\,1)\,2p_x\,(\beta\,2)\,d\tau_{1,2} \\ &= R_{\alpha\beta}\left\{1 + \frac{6}{D^2} - \frac{24}{D^4} - \frac{4401}{D^6} - \frac{5{,}111{,}505}{128\,D^8}\right\}, \end{aligned} \tag{A-7}$$

$$\begin{aligned} &\iint 2p_x\,(\alpha\,1)\,2p_z\,(\beta\,2)\,r_{12}\,2p_x\,(\alpha\,1)\,2p_z\,(\beta\,2)\,d\tau_{1,2} \\ &= R_{\alpha\beta}\left\{1 + \frac{9}{2\,D^2} - \frac{21}{4\,D^4} - \frac{26{,}379}{8\,D^6} - \frac{3{,}886{,}785}{128\,D^8}\right\}, \end{aligned} \tag{A-8}$$

where $D = \zeta\,R_{\alpha\beta}$.

It is also possible in the following way to obtain an estimate of the size of the terms that have been omitted. When $R_{\alpha\beta}$ becomes large, the quantities $(x_{\alpha 1}^2 + y_{\alpha 1}^2 + z_{\alpha 1}^2)$ and $(x_{\beta 1}^2 + y_{\beta 1}^2 + z_{\beta 1}^2)$ are both spherically symmetric, and the integral over the product of these should be the same as the integral over the product $2s^2\,(\alpha\,1)\,2s^2\,(\beta\,2)$. The asymptotic expansion for the integral involving all $2s$ orbitals is given below

$$\begin{aligned} &\iint 2s\,(\alpha\,1)\,2s\,(\beta\,1)\,r_{12}\,2s\,(\alpha\,1)\,2s\,(\beta\,2)\,d\tau_{1,2} \\ &= R_{\alpha\beta}\left\{1 + \frac{5}{D^2} - \frac{75}{4\,D^4} - \frac{2625}{D^6} - \frac{4{,}295{,}025}{128\,D^8}\right\}. \end{aligned} \tag{A-9}$$

This is to be compared with

$$\left(\tfrac{1}{9}\right) \iint \left[2p_z^2\,(\alpha\,1) + 2 \cdot 2p_x^2\,(\alpha\,1)\right] r_{12} \left[2p_z^2\,(\beta\,2) + 2 \cdot 2p_x^2\,(\beta\,2)\right] d\tau_{1,2}$$
$$= R_{\alpha\beta} \left\{ 1 + \frac{5}{D^2} - \frac{69.7}{4\,D^4} - \frac{2613}{D^6} - \frac{4{,}567{,}185}{128\,D^8} \right\}. \qquad \text{(A-10)}$$

Complete agreement in the terms containing D^{-4} and higher negative powers of D cannot be expected, since the term in $R_{\alpha\beta}^{-10}$ from (A-4), which has been omitted, contains a component which will contribute to the term in D^{-4}. However, an estimate of the error can be obtained from these differences. Since the error is likely to be largest in the D^{-4} term we can obtain a general error estimate by consideration of that term alone. When $D = 5$, the coefficients of D^{-4} in (A-9) and (A-10) differ by approximately $5.7/4(5)^4 = .002$. Furthermore, this error estimate is not simply the error of a single integral, but is the error of the weighted sum of three integrals, without cancellation of errors, since all of the signs are alike. Thus, it is more realistic to say that the actual error in the D^{-4} term for a given integral is approximately .0007, for $D = 5$. This means that these asymptotic expansions given above can be used to give integrals with errors less than 1%, even when the integrals involve the carbon-carbon bond distance for neighbors in benzene-like molecules, for then $D = 8$.

Finally, we consider the integral

$$\iint 2p_x\,(\alpha\,1)\,2p_x\,(\beta\,2)\,r_{12}\,2p_z\,(\alpha\,1)\,2p_z\,(\beta\,2)\,d\tau_{1,2}\,.$$

It can easily be seen by direct calculation that the first non-zero term which contributes to this integral is from the term in D^{-4}, and has a magnitude of $9/(16\,D^4)$. However, since it was estimated above that the error involved in the weighted sum of the integrals of (A-6), (A-7) and (A-8) was approximately $1.5\,D^{-4}$, it is clear that this integral is negligible, since its first non-zero contribution, and presumably the largest contribution, is smaller than the error of the weighted sum of the three integrals given above.

References

[*1*] Breit, G.: Physic. Rev. **34**, 553 (1929); **36**, 383 (1930); **39**, 616 (1932).
[*2*] Frost, A. A., and J. S. Braunstein: J. chem. Physics **19**, 1133 (1951).
[*3*] Hall, G. G., and A. Hardisson: Proc. Roy. Soc. **A 268**, 328 (1962).
[*4*] London, F.: J. Physics Radium 8, 397 (1937).
[*5*] Löwdin, P. O.: Advances in Physics **5**, 1 (1956).
[*6*] McWeeny, R.: Molec. Physics **1**, 311 (1958).
[*7*] Pariser, R., and R. G. Parr: J. chem. Physics **21**, 466 (1953).
[*8*] Parr, R.: J. chem. Physics **33**, 1184 (1960).
[*9*] Roothaan, C. C. J.: J. chem. Physics **19**, 1445 (1951).
[*10*] Shull, H., and G. G. Hall: Nature **184**, 1559 (1959).

(Received September 13, 1965)