SEPARATION OF THE LOCAL CONTRIBUTIONS TO THE TRANSITION MOMENTS AND THE POLARIZABILITY OF A MOLECULE IN THE SELF-CONSISTENT FIELD METHOD

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An unambiguous procedure for separating the contributions to the transition moment and dipole polarizability of a molecule has been achieved by introducing a universal transition operator for the coordinate, exhibiting invariant character with respect to a displacement of the origin of coordinates. The method has been illustrated for the calculation, in the self-consistent approximation, of the contributions of the fragments to the π-polarizability of a number of aromatic molecules in the singlet and triplet states. Definite transferability of the calculated local contributions from one molecule to another is observed.

The dipole polarizability α of a molecule can be represented as the sum of local contributions made by the separate structural elements of the molecules and a certain increment taking account of the interaction between the fragments. The fact that this increment is usually small demonstrates the additivity rule, which has long been familiar for this quantity (see, for example, [1, 2] and the up-to-date discussion in [3]).

The quantum-mechanical justification of the additive scheme for α encounters certain difficulties, associated with the usual representation of the polarizability α^{RR} in the direction R in the form of the sum with respect to excited states

$$\alpha^{RR} = 2\sum_{i}\frac{[Q^{R}_{(i)}]^2}{\lambda_i}, \tag{1}$$

where $Q^{R}_{(i)}$ is the moment of the transition from the ground state to the i-th excited state (with polarization R), and λ_i is the energy of excitation of this state. As a result, the separation of the local contributions in α^{RR} is closely related primarily to the breakdown of the moments of the transition into contributions corresponding to the separate fragments.

The formal difficulties which then arise can be illustrated for simplicity by specific examination of a π-electron model. In this case the usual equation for the moment of a transition polarized in the direction R, and related quantities (of the polarizability type), calculated in the approximation of singly excited configurations, reduces to

$$Q^{R} = \sqrt{2}\sum_{\mu=1}^{m}\sum_{j=1}^{n}\sum_{q=n+1}^{m} d_{qj}c_{\mu q}c^{*}_{\mu i}R_{\mu}. \tag{2}$$

Here, R_μ represents the diagonal matrix elements of the operator of the coordinate $\hat{R}$ in a basis of the AO $\{\chi_\mu\}_1^m$, where R_μ coincides with the coordinate of the atom at which the AO χ_μ is centered, d_{qj} represents the coefficients of the expansion of the excited or perturbed state with respect to the configurations $\Phi_{j\to q}$, and $c_{\mu j}$ represents the MO LCAO coefficients [4].

At first sight, it appears natural to identify the local contributions to Q^R for the entire molecule with the atomic quantities

$$\tilde{Q}^{R}_{\mu} = \sqrt{2}\Big(\sum_{q,j} d_{qj}c_{\mu q}c^{*}_{\mu j}\Big)R_{\mu}, \tag{3}$$

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which in the sum give $Q^R = \sum\limits_{\mu} \tilde{Q}^R_{\mu}$. These quantities have a significant disadvantage, however, associated with their noninvariant character with respect to the choice of the origin of coordinates in the molecule being studied. In fact,

$$\tilde{Q}^{R+a}_{\mu} = \tilde{Q}^R_{\mu} + a\sqrt{2}\sum_{j,q} d_{qj} c_{\mu q} c^*_{\mu j}$$

and only the sum of the resultant contributions $\sum\limits_{j,q} d_{qj} c_{\mu q} c^*_{\mu j}$ over all the AO χ_{μ} becomes zero as a consequence of the orthogonality of the occupied and unoccupied MO $\sum\limits_{\mu} c_{\mu q} c^*_{\mu j} = 0$, so that the integral value of Q^R remains invariant: $Q^{R+a} = Q^R$.

An attempt to obtain a general solution for problems of this kind was undertaken in [5], where relationships were proposed for calculating the local contributions to the dipole moment and polarizability, based on local systems of coordinates. The difference which then unavoidably arose between the total value of α^{RR} and the sum of the local one-center contributions is redistributed between the two-center contributions calculated by means of special numbers. The system of equations for these in the general case is indefinite, and this method does not give the unambiguous solution of the problem desirable for specific applications.

In the present work it has been possible, by introducing a transition operator of the coordinate invariant with respect to displacement, to put forward an unambiguous procedure for separating the local contributions to Q^R and α^{RR} and hence to follow the transferability of the calculated local contributions from one molecule to another.

TRANSITION OPERATOR OF THE COORDINATE, INVARIANT WITH RESPECT TO DISPLACEMENT

To find the invariant quantities $Q^R_{\mu} = Q^{R+a}_{\mu}$, we shall consider in general form an arbitrary transition moment Q^R in the form of the matrix element of the N-particle coordinate $R_N(1\ldots N) = \sum\limits_{i=1}^{N} R(i)$, calculated between the wavefunctions of the ground state $|\Phi(1\ldots N)\rangle$ and the excited state $|\Phi_*(1\ldots N)\rangle$

$$Q^R = \langle\Phi(1\ldots N)|R_N|\Phi_*(1\ldots N)\rangle \equiv \mathop{\mathrm{Sp}}_{(1\ldots N)} R_N|\Phi_*(1\ldots N)\rangle\langle\Phi(1\ldots N)|. \tag{4}$$

We then write Eq. (4) in the form of the trace of the one-electron operator R(1) and the one-particle density matrix of the transition $\tau(1)$ from $|\Phi\rangle$ into the state $|\Phi_*\rangle$

$$\tau(1) = N \mathop{\mathrm{Sp}}_{(2\ldots N)} |\Phi_*(1\ldots N)\rangle\langle\Phi(1\ldots N)|. \tag{5}$$

According to Eqs. (4) and (5), the moment of the transition is equivalent to the expression

$$Q^R = \mathrm{Sp} R\tau. \tag{6}$$

In Eq. (6) we redefine the operator of the coordinate in such a way that the new operator $\tilde{R}$ has the required property of invariant character with respect to a displacement by an arbitrary constant

$$\widetilde{R+a} = \tilde{R}. \tag{7}$$

For this purpose we subject R to a certain "oblique-angle" transformation

$$\tilde{R} = URV, \tag{8}$$

and the matrices of the transformation U, V are selected so as to satisfy automatically condition (7) and the additional natural requirement

$$Q^R = \mathrm{Sp}\tilde{R}\cdot\tau, \tag{9}$$

that is so that the new operator can be used to calculate the transition moments from the previous relationship (6). From Eq. (7) we readily obtain the operator equation

$$UV = 0, \tag{10}$$

and it follows from Eq. (9) that the one-electron transition matrix should also be invariant in a transformation of type (8)

$$V\tau U = \tau. \tag{11}$$

The specific structure of U, V is determined, if it can be found, by the form of the wavefunctions $|\Phi\rangle$, $|\Phi_*\rangle$ and the corresponding density matrices.

In the case of greatest interest to us, that is in the case of the one-determinant Hartree–Fock description of the ground state $|\Phi\rangle$ and the excited or perturbed state $|\Phi_*\rangle$ in the form of the superposition $\sum_{j,q} d_{qj}\Phi_{j\to q}$, the one-particle spin-free transition density matrix has the form

$$\tau = \sqrt{2}\sum_{j,q} d_{qj}\,|\varphi_q\rangle\langle\varphi_j|, \tag{12}$$

where $|\varphi_j\rangle$ denotes the MO occupied in the ground state, and $|\varphi_q\rangle$ represents a vacant MO.

It follows from Eq. (11) that τ is invariant with respect to the projection of τ on the left into unoccupied MO and on the right into occupied MO. The projector on to the occupied MO, which is the familiar Fock–Dirac density matrix, is denoted by $\rho = \sum_{j=1}^{n} |\varphi_j\rangle\langle\varphi_j|$. The projector on to the unoccupied MO $\sum_{q=n+1}^{m} |\varphi_q\rangle\langle\varphi_q|$ then coincides with $I - \rho$, since from the completeness conditions, $\sum_{i=1}^{m} |\varphi_i\rangle\langle\varphi_i| = I$. Thus

$$\tau = (I - \rho)\tau\rho. \tag{13}$$

Comparing with Eqs. (13) and (11), we assume the identities $U = \rho$, $V = I - \rho$, and with this choice, because of the idempotent character of ρ, Eq. (10) is satisfied automatically. As a result, we have $\tilde{R} = \rho R(I - \rho)$. It is more convenient to work with Hermitian operators, so that the symmetrized operator $\tilde{R}$ can be written as

$$\tilde{R} = \rho R(I - \rho) + (I - \rho)R\rho = 1/2(R - YRY),$$

where $Y = 2\rho - I$, and the symmetrized transition density matrix is $\frac{1}{2}(\tau + \tau^+) \equiv D$. We have finally

$$\tilde{R} = 1/2(R - YRY), \tag{14}$$

$$Q^R = \mathrm{Sp}\,\tilde{R}\tau = \mathrm{Sp}\,\tilde{R}D. \tag{15}$$

It may be noted that the component of the polarizability α^{RR} in the direction R can also be written by means of Eq. (15), but in this case

$$\alpha^{RR} = \mathrm{Sp}\,\tilde{R}\cdot\delta Y, \tag{16}$$

where δY is the correction to the density matrix of the ground state satisfying the non-homogeneous equation, the right hand side of which also contains the matrix $\tilde{R}$ [6].

LOCAL COMPONENTS OF THE TRANSITION MOMENT

We can now consider specifically the problem of separating the local contributions to the transition quantities Q^R or α^{RR} in the prepared form (15) and (16). For this purpose we break down the molecule into two parts, A and B. This breakdown corresponds to the following block structure of the matrices:

$$R = \begin{Vmatrix} R_A & 0 \\ 0 & R_B \end{Vmatrix}, \quad D = \begin{Vmatrix} D_A & D_{AB} \\ D_{BA} & D_B \end{Vmatrix}, \quad Y = \begin{Vmatrix} Y_A & Y_{AB} \\ Y_{BA} & Y_B \end{Vmatrix}. \tag{17}$$

Because of the involute character of $Y^2 = I$, the following restrictions are imposed on the blocks Y

$$Y_A^2 + Y_{AB}Y_{BA} = I, \quad Y_{AB}Y_B + Y_AY_{AB} = 0. \tag{18}$$

The transition operator of the coordinate (14) is then detailed as follows:

$$\widetilde{R}_A = 1/2(R_A - Y_A R_A Y_A - Y_{AB} R_B Y_{BA}), \tag{19}$$

$$\widetilde{R}_B = (\widetilde{R}_A)_{A\leftrightarrow B}, \quad \widetilde{R}_{AB} = 1/2(Y_{AB} R_B Y_B + Y_A R_A Y_{AB}). \tag{20}$$

The total moment Q^R then breaks down into the local contributions Q^R_A and Q^R_B and the inter-fragment component Q^R_{AB}

$$Q^R = Q^R_A + Q^R_B + Q^R_{AB}, \tag{21}$$

$$Q^R_A = \mathrm{Sp}\,\widetilde{R}_A D_A, \quad Q^R_B = \mathrm{Sp}\,\widetilde{R}_B D_B, \tag{22}$$

$$Q^R_{AB} = \mathrm{Sp}\,(\widetilde{R}_{AB} D_{BA} + \widetilde{R}_{BA} D_{AB}). \tag{23}$$

As a consequence of the involute conditions (18), the relationships $(\widetilde{R + aI})_A = \widetilde{R}_A$, $(\widetilde{R + aI})_{AB} = \widetilde{R}_{AB}$, and hence the requirements of invariant character

$$Q^{R+a}_A = Q^R_A, \quad Q^{R+a}_{AB} = Q^R_{AB} \tag{24}$$

are fulfilled.

An analysis of the transition matrix D from the viewpoint of the local character of the electronic transitions was carried out in [8], where it was shown that the norms $\|D_A\|$, and $\|D_B\|$ can be used to estimate the localization of the excitation on the fragments A and B, respectively, and that $\|D_{AB}\|^2$ can be used to estimate the weighting of the states with charge transfer. From this viewpoint, the breakdown (21)-(23) is quite natural.

The situation with the inter-fragment interaction Q^R_{AB} is characteristic. From the quasidiagonal structure of R in Eq. (17), it can readily been seen that the previous expression for Q^R of type (6) leads to

$$Q^R = \mathrm{Sp}\,R_A D_A + \mathrm{Sp}\,R_B D_B, \tag{25}$$

so that the states with charge transfer, defined by the block D_{AB}, do not make a contribution to the transition moment. In the new invariant representation of the contributions to Q^R there has appeared the inter-fragment transition moment (23), generated directly by the matrix D_{AB}. This dependence of Q^R_{AB} on D_{AB} can be eliminated by using the relationship $D + YDY = 0$, equivalent to Eq. (13). This identity leads to the following relationship between the block D_A and D_{AB}

$$D_A + Y_A D_A Y_A + Y_A D_{AB} Y_{BA} + Y_{AB} D_{BA} Y_A + Y_{AB} D_B Y_{BA} = 0 \tag{26}$$

and makes it possible to transform Eq. (23) to the form

$$Q^R_{AB} = \frac{1}{2}\,\mathrm{Sp}\,D_A\,(R_A + Y_A R_A Y_A + Y_{AB} R_B Y_{BA}) + \frac{1}{2}\,\mathrm{Sp}\,D_B\,(R_B + Y_B R_B Y_B + Y_{BA} R_A Y_{AB}), \tag{27}$$

in which D_{AB} and D_{BA} are eliminated in explicit form. We can compare Eq. (27) with the quantities in Eq. (22), which for clarity can be written in the expanded form

$$\begin{aligned} Q^R_A &= \frac{1}{2}\,\mathrm{Sp}\,D_A\,(R_A - Y_A R_A Y_A - Y_{AB} R_B Y_{BA}), \\ Q^R_B &= \frac{1}{2}\,\mathrm{Sp}\,D_B\,(R_B - Y_B R_B Y_B - Y_{BA} R_A Y_{AB}). \end{aligned} \tag{22'}$$

The terms with Y in Eqs. (27) and (22') differ in sign, so that the result in the sum gives Eq. (25), with the difference that $\mathrm{Sp}\,R_A D_A$ and $\mathrm{Sp}\,R_B D_B$ in Eq. (25) are not invariant, since in the general case, $\mathrm{Sp}\,D_A \neq 0$, although $\mathrm{Sp}\,D = \mathrm{Sp}\,D_A + \mathrm{Sp}\,D_B = 0$. The presence in Q^R_A of terms with $Y_{AB} R_B Y_{BA}$ indicates that the local component Q^R_A absorbs a certain fraction of the interaction of the fragment A with the rest of the molecule. A rigorous separation takes place in the case of a weak interaction between the fragments, a measure of which is provided by $\|Y_{AB}\|$ (smallness of the orders of the bonds between the fragments). By assuming that Y_{AB} is a matrix of the first order of smallness with respect to the inter-fragment interaction, we find that

$$Q^R_A \approx \frac{1}{2}\,\mathrm{Sp}\,D_A\,(R_A - Y_A R_A Y_A) \tag{28}$$

with an accuracy up to second order. The actual inter-fragment contribution Q^R_{AB} is then of the second order of smallness. This feature apparently determines the real possibility of breaking down the oscillator strength and polarizability into local contributions in those cases where it is possible to distinguish weakly interacting fragments in the molecule.

We have thus shown that in the calculation of Q_A^R and Q_B^R it is possible to use local systems of coordinates, centered on the fragments A and B, respectively, but in this case it is necessary to use Eqs. (22) and (22').

BREAKDOWN OF THE POLARIZABILITY

We can now detail the relationships found as applied to the analysis of the polarizability α^{RR} of the form (16), for which we expand the correction δY with respect to the transition density matrices $D^{(i)}$ ([6], pp. 235, 236),

$$\delta Y = 2\sum_i \frac{\mathrm{Sp}\, D^{(i)}R}{\lambda_i} D^{(i)} = 2\sum_i \frac{Q_{(i)}^R}{\lambda_i} D^{(i)}. \tag{29}$$

The analogous expansion for $\tilde{R}$ gives

$$\widetilde{R} = \sum_i Q_{(i)}^R D^{(i)}. \tag{30}$$

By now breaking down $D^{(i)}$, the density matrix of the transition into the i-th excited state, into blocks and introducing the symbols

$$l_{\mathrm{A}}^{(i)} = \mathrm{Sp}\,[D_{\mathrm{A}}^{(i)}]^2, \qquad l_{\mathrm{AB}}^{(i)} = 2\,\mathrm{Sp}\, D_{\mathrm{AB}}^{(i)} D_{\mathrm{BA}}^{(i)}, \tag{31}$$

$$l_{\mathrm{A}}^{(ij)} = \mathrm{Sp}\, D_{\mathrm{A}}^{(i)} D_{\mathrm{A}}^{(j)}, \quad l_{\mathrm{AB}}^{(ij)} = \mathrm{Sp}\big[D_{\mathrm{AB}}^{(i)} D_{\mathrm{BA}}^{(j)} + D_{\mathrm{AB}}^{(j)} D_{\mathrm{BA}}^{(i)}\big], \tag{32}$$

we obtain the following representation of the local and inter-fragment components of the polarizability of the type (21)-(23)

$$\alpha^{RR} = \alpha_{\mathrm{A}}^{RR} + \alpha_{\mathrm{B}}^{RR} + \alpha_{\mathrm{AB}}^{RR}, \tag{33}$$

$$\alpha_{\mathrm{A}}^{RR} = 2\sum_i \frac{[Q_{(i)}^R]^2}{\lambda_i}\, l_{\mathrm{A}}^{(i)} + 2\sum_{i\neq j} \frac{Q_{(i)}^R Q_{(j)}^R}{\lambda_i}\, l_{\mathrm{A}}^{(ij)}, \tag{34}$$

$$\alpha_{\mathrm{AB}}^{RR} = 2\sum_i \frac{[Q_{(i)}^R]^2}{\lambda_i}\, l_{\mathrm{AB}}^{(i)} + 2\sum_{i\neq j} \frac{Q_{(i)}^R Q_{(j)}^R}{\lambda_i}\, l_{\mathrm{AB}}^{(ij)}. \tag{35}$$

The localization numbers $l_A^{(i)}$ and $l_{AB}^{(i)}$ arose earlier [8], where they characterized the local character of the i-th excitation and hence the degree of charge transfer. From the normalization $\mathrm{Sp}\ D^2 = 1$ we have $l_A^{(i)} + l_B^{(i)} + l_{AB}^{(i)} = 1$. The new numbers (32) characterize the overlap of the excitations, and as a consequence of the orthogonal character of the excited states $\mathrm{Sp}\ D^{(i)}\ D^{(j)} = 0$, their sum becomes zero: $l_A^{(ij)} + l_B^{(ij)} + l_{AB}^{(ij)} = 0$. As a consequence of this condition, the terms with $l_{AB}^{(ij)}$, etc. do not appear in the overall polarizability, which reduces to the standard expression (1).

The possible identification of α_A^{RR} with

$$\alpha_{\mathrm{A}}^{RR} = 2\sum_i \frac{[Q_{(i)}^R]^2}{\lambda_i}\, l_{\mathrm{A}}^{(i)} \tag{36}$$

which is suggested by Eqs. (1) and (34), is also an acceptable version of the separation of the local contribution in the total polarizability, but this method requires a knowledge of all excited states possible in the given scheme and their characteristics. At the same time, Eqs. (34) and (35) are based on the use of the quantities (16) and (21)-(23), the calculation of which requires a knowledge of only the total correction δY, which is usually found numerically, avoiding the expansion of type (29).

It is obvious that when there are more than two fragments A, B, ..., C, the local contributions and the inter-fragment components are calculated from equations of the same type as Eqs. (22) and (23)

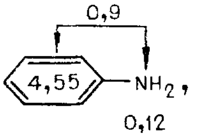
$$\alpha_{\mathrm{A}}^{RR} = \mathrm{Sp}\, \widetilde{R}_{\mathrm{A}} \delta Y_{\mathrm{A}}, \ \ldots, \ \alpha_{\mathrm{C}}^{RR} = \mathrm{Sp}\, \widetilde{R}_{\mathrm{C}} \delta Y_{\mathrm{C}},$$
$$\alpha_{\mathrm{AB}}^{RR} = \mathrm{Sp}\, (\widetilde{R}_{\mathrm{AB}} \delta Y_{\mathrm{BA}} + \widetilde{R}_{\mathrm{BA}} \delta Y_{\mathrm{AB}}) \ldots. \tag{37}$$

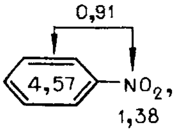
TABLE 1. Local Components of the Average π-Polarizability, Å³, in a Series of Polyphenyls

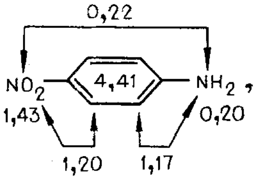
Molecule	Ground state				Lowest triplet			
	A	α_A	AB	α_{AB}	A	α_A	AB	α_{AB}
Biphenyl	1	4,9	1—2	1,8	1	8,8	1—2	3,0
Terphenyl	1	5,1	1—2	2,1	1	9,6	1—2	8,6
	2	5,1	1—3	0,3	2	5,6	1—3	1,2
Quaterphenyl	1	5,2	1—2	2,3	1	9,0	1—2	10,9
	2	5,3	2—3	2,5	2	10,4	2—3	6,6
			1—3	0,4			1—3	3,2
			1—4	0,5			1—4	0,5

In CNDO calculations, the matrix R is not purely diagonal, but retains a block structure of the form (17) for any breakdown of the molecule into fragments, so that Eqs. (19)-(37) also cover the case of all valence electrons.

As an illustration we give the results of calculations of the local contributions to the π-electron polarizability for a number of aromatic molecules. For the average polarizability of various benzene derivatives it is possible to use the following diagrams (α in Å³):







where the numbers in the ring or at the substituent correspond to the local contributions α_A, and the numbers above the arrow coincide with the value of the inter-fragment contribution α_{AB}. It can be seen that the average π-polarizability of the benzene ring is with good accuracy a transferable quantity, although for separate components of the polarizability this stability of the values of the local contributions is not observed. For example, in benzene $\alpha^{xx} = \alpha^{yy} = 6.74$ Å³, whereas in aniline, for the phenyl ring, $\alpha^{xx}_{Ph} = 7.14$ Å³, $\alpha^{yy}_{Ph} = 6.51$, and in nitroaniline, $\alpha^{xx}_{Ph} = 7.50$, $\alpha^{yy}_{Ph} = 5.74$.

Polyphenyls in the ground singlet state are also characterized by almost transferable values of α_{Ph}, and the whole effect of strong nonadditivity for the polarizability of these conjugated systems can be assigned to the inter-fragment component $\alpha_{Ph,Ph'}$, which for the nearest interactions are also almost transferable; the long-range interactions are small and can be neglected. In the lowest triplet state (the calculation was carried out in the unrestricted Hartree—Fock (UHF) approximation by the method described in [8]), the transferability of the π-contributions, which are greater in this case, to the polarizability is much lower than that for the singlet case. The results of the calculation of α_A and α_{AB} for polyphenyls are given in Table 1, where the usual numbering of the fragments is adopted (from the start of the polyphenyl chain).

In summarizing the foregoing, we would emphasize the simplicity of this method for separating the local contributions from the calculated values of α^{RR}. With slight changes, the same method can be used for the hyperpolarizability β^{RST}, the coefficient for the third power of the electric field strength $\vec{\mathscr{E}}$ in the expansion of the energy of a molecule in a series with respect to the powers of $\mathscr{E}$. Invariant character in this case is achieved by the identity transformation of the quantity β of the form [6]

$$\beta = \mathrm{Sp}\, \delta f (\delta Y)^2 Y \equiv \mathrm{Sp}\, B \cdot \delta Y,$$

where $B = {}^1/_2[[\delta f, Y]_+, \delta Y]_+$. It can be seen that the addition of the displacement of the coordinate aI to the correction δf of the Fock operator f leads, with an accuracy corresponding to the coefficient a, to the quantity $[Y, \delta Y]_+$, which becomes zero [6], and this ensures the required invariant character of the operator B.

The separation of the local contributions to the electrical properties of molecules, in addition to the obvious application to the problem of additivity, may also prove useful in the study of the instability of a molecule in an electric field, leading to the separation of definite molecular fragments [9]. With an accuracy corresponding to the terms $\mathscr{E}^3$, the electrostatic energy concentrated in the fragment is estimated as the sum of the corresponding local contributions to the dipole moment, polarizability, and hyperpolarizability.

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A QUANTUM-CHEMICAL STUDY OF THE REACTION OF CARBON MONOXIDE MOLECULES WITH THE ATOMS AND IONS OF THE ELEMENTS OF THE SECOND PERIOD.

II. CALCULATION FOR THE COMPLEXES $Be^{2+}\cdot CO$ AND $Be\cdot CO$

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The Fischer–Kollmar version of the CNDO method has been used to study the geometric and electronic structure of the systems $Be^{2+}\cdot CO$ and $Be\cdot CO$. For the first of these, the most favorable geometric configuration corresponds to the linear arrangement of the atoms, and for $Be\cdot CO$ the most favorable configuration corresponds to the triangular arrangement. The calculations indicate that the CO molecule forms strong bonds both with the beryllium atom and with the beryllium cation (∿80 and 180 kcal/mole, respectively). In the complex $Be^{2+}\cdot CO$, the strength of the C–O bond is of the same order as the strength of the Be–CO bond, that is, $Be^{2+}\cdot CO$ is a three-component system with linkages of approximately equal strength, characterized by high values of the energy of rupture. The calculations indicate that the interaction of the CO molecule with the beryllium atom lowers the characteristics of its excitation process, and hence should soften the conditions required for its activation.

The carbon monoxide molecule in many respects deserves greater attention. In particular, it is the most stable diatomic molecule (its dissociation energy is 256 kcal/mole [1]), and this is stimulating the search for possible applications of carbon monoxide as a component in materials science. At the same time, as already noted in [2], carbon monoxide is a harmful (toxic) byproduct of many technological processes, particularly those associated with the combustion of organic fuel, and in principle, the problem of developing absorbers for this gas is urgent. This to some extent explains the interest in the study of such problems as the strength of the bonds formed by CO molecules with the atoms or ions of various elements, the value of the coordination number in complexes of the type $X(CO)_n$, the

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