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Semiempirical Quantum Chemical Calculations of Molecular π-Complexes

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A method is suggested to calculate the geometrical and thermodynamical characteristics of organic π-complexes. The interaction energy is considered as a sum of two terms: the specific quantum chemical interaction of the π-electron systems depending essentially on the chemical nature of reactants, and the nonspecific atom–atom (van-der-Waals) interaction depending only on the kind of atoms belonging to the fragments of a complex. An attractive quantum chemical interaction is described in terms of the PPP-method; the van-der-Waals interaction is expressed in terms of the empirical exp-6-potential. The geometries of complexes are found by the complete energy minimization with respect to six parameters characterizing the mutual orientation of the complex fragments. Energies, entropies and equilibrium constants of several tetracyanoethylene π-complexes are calculated by this method. The results agree satisfactorily with experimental data.

Key words: Intermolecular interactions – Molecular complexes – Calculations of geometry and thermodynamical properties of complexes.

1. Introduction

Theoretical study of the structure of molecular complexes is of significant interest. Up to now it has been performed, as a rule, on a qualitative quantum chemical level [1]. The calculation using an empirical atom–atom scheme involving electrostatic interactions has been also reported [2]. Only for a few small molecules some *ab initio* calculations have been published [3–5].

Typical organic complexes are rather complicated polyatomic species. Their computation needs optimization of intermolecular geometrical parameters since

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the geometrical structure is unknown. For such a computation a semiempirical theory seems appropriate. However, the existing standard semiempirical computational techniques based on the ZDO approximation fail to be valid in this case, as a result of the inconsistent treatment of the nonorthogonality effects [6, 7], one of the main components of the intermolecular interaction energy. Therefore, it is not surprising that the formation energy of the benzene-tetracyanoethylene (TCNE) complex obtained by the CNDO/2 procedure [8] (125 kcal/mole) greatly exceeds the experimental value (5.5–7.5 kcal/mole) [9, 10], the calculated intermolecular distance (1.75 Å) being quite unrealistic. Similar observations have been reported recently [11].

Some successful CNDO/2 computations of small molecular complexes have been published [12], introducing the intermolecular nonorthogonality effects and the dispersion interaction in the framework of SCF perturbation theory [13]. In the present communication we suggest an alternative semiempirical method for the calculation of π-complexes. It is based on the "almost π-electron approximation".

The analysis of interactions between π-electron molecules has naturally revealed the term corresponding to the interaction of π-electron systems, calculating this term just in the ZDO approximation [6]. That is the so called stabilization energy (SE), the main chemically specific component of the interaction. As calculated by a SCF method (i.e. in fact, by the PPP method), the SE includes the effects of "chemical bonding" and the main electrostatic effects. The overall interaction energy is obtained after supplementing the SE by nonspecific additive terms: the repulsion term caused by the nonorthogonality of wavefunctions of the separated complex fragments, and also the attractive dispersion interaction. These additional energy contributions will be referred to as the "van-der-Waals interaction" below. They depend on all valence electrons, σ-electrons taking a principal part, since most of the valence electrons are σ-electrons. It is important to emphasize that the nonorthogonality effects and dispersion forces for π-electrons are missing in PPP calculations. That is the reason why the calculation of van-der-Waals interaction simultaneously for all valence electrons, without separating the σ- and π-components, is a consistent procedure.

The "almost π-electron approximation" has been used earlier for studying some chemical reactions of π-electron systems [14]. As applied to calculations of π-complexes, the computational procedure is simplified significantly, since it is not necessary to take the changes of AO hybridization into account. In contradistinction to previous works, the nonspecific van-der-Waals contribution is treated here in terms of an empirical atom–atom scheme. The procedure of the rather similar type has been suggested to calculate the interaction of two benzene molecules [15].

2. Experimental Characteristics of π-Complexes

The summary of experimental data on equilibrium constants of some π-complexes of TCNE listed in Tables 1–3 elucidates some problems arising in the

Table 1. Thermodynamic constants of TCNE-benzene complex in different solvents

K(22°C) $1 \cdot mole^{-1}$	$-\Delta F$ $kcal \cdot mole^{-1}$	$-\Delta H$ $kcal \cdot mole^{-1}$	$-\Delta S$ $cal \cdot mole^{-1} deg^{-1}$	Solvent method	Ref.
0.108	−1.32	3.16	15.02	CH_2Cl_2 calorimeter	10
0.129	−1.21	2.30	12.6	CH_2Cl_2 spectral	16
2.00	0.41	2.30	6	CH_2Cl_2 spectral	17
0.14	−1.15	1.89	10.28	CH_2Cl_2 spectral	18
0.34	−0.64	2.59	10.95	$CHCl_3$ spectral	18
0.73	−0.19	3.24	11.65	CCl_4 spectral	18
1.42	0.21	4.03	12.92	cyclohexene spectral	18
2.37	0.51	4.33	12.95	benzene spectral	18

Table 2. Thermodynamic constants of TCNE complexes with methylbenzenes in the gas phase [19] and in solution (CH_2Cl_2) [16]

	Gas phase			Solution		
Donor	K(25°C) $1 \cdot mole^{-1}$	$-\Delta H$ $kcal \cdot mole^{-1}$	$-\Delta S$ $cal \cdot mole^{-1} deg^{-1}$	K(25°C) $1 \cdot mole^{-1}$	$-\Delta H$ $kcal \cdot mole^{-1}$	$-\Delta S$ $cal \cdot mole^{-1} deg^{-1}$
p-Xylene	280	8.1	15.5	7.2	3.37	7.38
Mesitylene	1020	9.9	18.7	16.0	4.52	9.61
Durene	11800	10.8	17.3	49.5	5.07	9.23

Table 3. Thermodynamic constants of TCNE complexes with aromatic donors in solution (CH_2Cl_2)

Donor	K(22°C) $1 \cdot mole^{-1}$	$-\Delta H$ $kcal \cdot mole^{-1}$	$-\Delta S$ $cal \cdot mole^{-1} deg^{-1}$	Ref.
Benzene	0.108	3.158	15.02	10
Naphthalene	0.247	4.364	17.41	10
Phenanthrene	1.874	11.34	36.79	10
Pyrene	0.888	4.530	15.43	10
Biphenylene	0.710	2.6	4.1	20
Fluorene	19	4.0	7.8	21

course of their interpretation. Experiments are usually performed in solution. Equilibrium constants, K, as measured by different methods in various solvents, may differ by a factor of order 10. The measured enthalpies, ΔH, and entropies, ΔS, of formation display irregularities which are minimized when passing to the free energies, ΔF, due to the compensation effect. A few gas-phase data [18] show that the free complexes seem to be more stable than the dissolved ones. And finally, as the observed characteristics of interaction are small, the relative contribution coming from temperature dependent effects may be significant. These effects are neglected in a standard quantum-chemical treatment dealing with states at 0°K. Thereby, since one is attached to the liquid-phase room-temperature experiments, the incorporation of some elements of empirical adjustment in a calculation procedure is inevitable. In such a situation a simple semiempirical method has certain advantages.

3. Calculation Technique

3.1. Geometry

The energy of the intermolecular interaction of the fragments is essentially less than the intramolecular one. Therefore, in good approximation, the fragment geometry coincides with that of the isolated reactants. This allows to describe the geometry of a complex in terms of only six parameters: intermolecular distance r and angles θ_1, θ_2, θ_3, φ_1, φ_2 determining the mutual orientation of fragments (Fig. 1). The geometry of a complex should be obtained by the complete energy optimization with respect to those parameters.

3.2. Energy

The following master formula was used for calculations of interaction energy

$$U = \Delta_\pi + U_V. \quad (1)$$

The π-electron SE, Δ_π, describes the specific quantum-chemical interaction of the complex fragments and depends on their chemical nature; U_V describes the nonspecific van-der-Waals interaction and depends only on the kinds of atoms entering the fragments. In order to compute U_V we adopt the atom–atom scheme

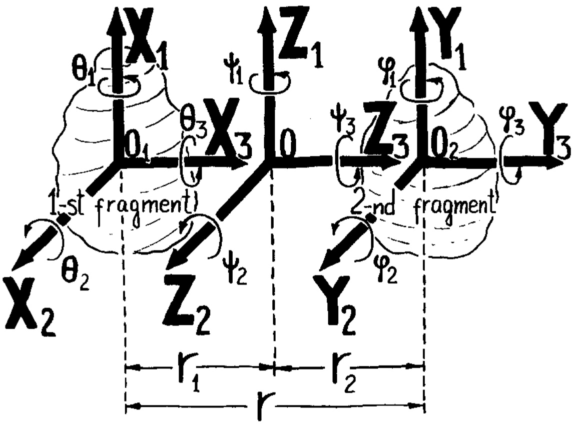

Fig. 1. Parameters determining the orientation of the complex fragments and the rotation of whole complex: θ_1, θ_2, θ_3; φ_1, φ_2, φ_3 and ψ_1, ψ_2, ψ_3 are rotation angles of the first and second fragments and of the whole complex around the respective space-fixed coordinate axes located at their centers of mass. If $G(\theta_i)$ is the operator of rotation by θ_i around the axis X_i, then generally it is accepted that $G(\theta_1, \theta_2, \theta_3) = G(\theta_2)G(\theta_1)G(\theta_3)$ (and, similarly for other rotations in the systems $\{Y_i\}$ and $\{Z_i\}$). For other notation and details see Appendix

using the empirical exp-6-potential

$$U_V = \sum_{r,s} \{-A_{rs} r_{rs}^{-6} + B_{rs} \exp(-C_{rs} r_{rs})\}. \tag{2}$$

The summation is carried out over pairs of atoms r and s belonging to different fragments.

The Δ_π has been computed by the PPP method. Matrix elements of π-electron Fockian f_{rs} are:

$$f_{rr} = W_r + \tfrac{1}{2} p_{rr} \gamma_r + \sum_{k \neq r} (p_{kk} - N_k) \gamma_{rk}$$

$$f_{rs} = h_{rs} - \tfrac{1}{2} p_{rs} \gamma_{rs}$$

(if r and s are the neighbouring atoms of the same molecule or if they belong to different molecules)

$$f_{rs} = -\tfrac{1}{2} p_{rs} \gamma_{rs}$$

(if r and s are nonneighbouring atoms of the same molecule)

$$\gamma_{rs} = e^2 \{(e^2/\gamma_r \gamma_s)^2 + r_{rs}^2\}^{-1/2}; \qquad h_{rs} = k_{rs} S_{rs}.$$

Here S_{rs}, p_{rs} and r_{rs} are the corresponding overlap integral, bond order and intermolecular distance, N_k is the number of electrons on the p_π-AO of atom k, and e is the electron charge. We used the following values for the parameters: $W_C = -11.16$ eV; $W_N = -14.17$ eV; $\gamma_C = 11.13$ eV; $\gamma_N = 12.34$ eV; $k_{CC} = -9.77$ eV; $k_{CN} = -10.13$ eV. The geometries of fragments were not optimized; the experimental data on bond lengths and valence angles were used.

All contacts of all π-AOs with account of their mutual orientation were included for intermolecular interactions.

The standard SCF iterative procedure for systems under investigation was observed to diverge (the amplitudes of energy oscillations were about 0.5 eV). In

Table 4. Parameters of the exp-6-potential (2). (A in kcal · Å^6 · mole^{-1}; B in kcal · mole^{-1}; C in Å^{-1})

	Present work			Ref. [25]		
Atoms	A	B	C	A	B	C
C—C	280	70 000	3.63	331	47 000	3.63
C—N	280	70 000	3.63	–	–	–
C—H	100	60 000	4.32	117	47 000	4.32
N—H	100	60 000	4.32	–	–	–
H—H	30	50 000	5.18	41	47 000	5.18

order to achieve convergence the "level-shifting" method [22, 23] was applied, the theoretical background of which has been clarified in the recent review [24]. This method provided excellent convergence ($\sim 10^{-7}$ eV with respect to energy) in a few iterations.

Computations of van-der-Waals energy U_V using the parameters of exp-6-potential recommended by Caillet and Chaverie [25] yielded 6.3 kcal/mole for the energy of the TCNE-benzene complex. This value is typical for the gas-phase equilibrium (see Table 2). We considered the coefficients A_{rs} and B_{rs} of potential (2) as adjustable parameters changing them in such a way that the results of computations reproduced experimental data on the formation enthalpies of the complexes of TCNE with aromatic donors in solution (Table 3). Thus, the solvation and temperature effects were implicitly incorporated in the new values presented in Table 4.

3.3. *Equilibrium Constants*

Equilibrium constants, K, for the process described as $A + B \rightleftarrows C$ were calculated according to the standard formula

$$K = \frac{Q_C}{Q_A Q_B} \exp\left(-\frac{U}{RT}\right)$$

where Q_A, Q_B and Q_C are the corresponding partition functions. So we made no distinction between the experimental enthalpies of formation ΔH and the calculated interaction energies U. The partition functions were calculated as a product of elementary partition functions for separate degrees of freedom. The following model was accepted: the fragments of a complex were considered as rigid and their mutual motions were considered as small-amplitude vibrations near the equilibrium point. The first condition allows to describe a complex by only twelve independent variables instead of $3N$ cartesian coordinates (N is the number of atoms in a complex). Separating the center of mass translations reduces their number to nine. It is convenient to start with the following initial set of coupled coordinates (see Fig. 1):

$$\begin{array}{llll} q^1=\theta_1 & q^4=\varphi_1 & q^6=r & q^7=\psi_1 \\ q^2=\theta_2 & q^5=\varphi_2 & & q^8=\psi_2 \\ q^3=\theta_3 & & & q^9=\psi_3. \end{array} \tag{3}$$

In a small amplitude approximation for vibrations one can present the Hamiltonian of the system in a form

$$H=H_0+\tfrac{1}{2}g_{\mu\nu}\dot{q}^{\mu}\dot{q}^{\nu}+\tfrac{1}{2}k_{\mu\nu}q^{\mu}q^{\nu} \tag{4}$$

where $g_{\mu\nu}$ are the elements of the kinetic energy matrix, $k_{\mu\nu}$ represent the matrix of potential energy, and H_0 is the equilibrium energy of a system; the dots designating the time derivatives. Here tensor notations are used (covariant and contravariant indices, summation over repeating indices).

Elements of the matrix $k_{\mu\nu}$ are available from the numerical differentiation of the energy of a complex calculated in terms of coordinates $\{q^{\nu}\}$. Calculation was encumbered by the fact that the dependence of energy (1) on angular variables showed fast irregular oscillations of small amplitude ($\sim 10^{-2}$ eV). This difficulty has been overcome after smoothing the function (1) by averaging over a sufficiently large energy interval.

The kinetic energy matrix for the geometrical model of a complex accepted above cannot be obtained by the regular procedure [26]. An account of its calculation is given in the Appendix. Solving the vibrational problem for the Hamiltonian (4) allows to obtain the frequencies of normal modes and to calculate the corresponding vibrational partition functions.

Our computations showed that the energy of a complex is almost independent of the angle θ_3. This result indicated that the internal rotation of the fragments around the Z_3 axis (see Fig. 1) is practically free. The vibrational partition function for this degree of freedom was calculated as that of the free rotation.

The internal motions of fragments and the overall rotations of the complex as a whole are mixed in the coordinates $\{q^{\nu}\}$. Solving the vibrational problem separates three purely rotational modes with zero frequencies.

4. Results and Discussion

The result of our calculations of geometrical and thermodynamical characteristics of some complexes of TCNE are presented in Table 5. The comparison of Tables 3 and 5 shows that the calculated values of the energies of the complex formation agree satisfactorily with experimental data (phenantrene presents the single exception but that seems to be an experimental error). Nevertheless, the equilibrium constants are systematically lowered by a factor of about ten. Our explanation is that the harmonic approximation (4) overestimates the rigidness of complexes. One can anticipate that inclusion of the anharmonicity correction in

Table 5. The calculated intermolecular distances, thermodynamical parameters and frequencies of normal modes for some π-complexes TCNE and aromatic donors. (r in Å, energies in kcal · mole^{-1}, entropies in cal · mole^{-1} deg^{-1}, constants in l · mole^{-1}, frequencies in cm^{-1})

		Thermodynamical parameters					Frequencies of some normal modes		
Donor	r	K(25°C)	$-U$	$-\Delta_\pi$	$-U_V$	$-\Delta S$	$\omega_{\max}$	ω_r	$\omega_{\min}$
Benzene	3.49	0.013	2.8	1.0	1.8	18	68	59	26
Naphthalene	3.43	0.019	4.0	1.8	2.1	21	64	59	37
Anthracene	3.45	0.063	4.4	1.5	2.9	20	58	54	28
Phenantrene	3.47	0.031	4.6	1.9	2.7	22	59	56	31
Pyrene	3.47	0.109	5.0	2.0	3.0	21	55	55	28
Biphenylene	3.50	0.042	4.0	1.7	2.3	20	60	53	21
Fluorene	3.50	0.012	4.4	1.7	2.7	23	58	55	29

the calculation of partition functions would change the values of the preexponential factors in the right direction without changing the exponent indices. This defect cannot be eliminated by readjusting the parameters of the potential (2). Modifying their values to fit the equilibrium constants alters the energies significantly. In particular, by changing the parameters we obtained either $K = 0.037$ l/mole and $U = -4.0$ kcal/mole or $K = 0.36$ l/mole and $U = -6.3$ kcal/mole for benzene.

The relative contributions from the π-electron SE, Δ_π, and van-der-Waals term, U_V, seem to be typical for weak complexes. The same can be said about the vibrational frequencies. The maximal and minimal frequencies and that characterizing the "valence" vibration with respect to parameter r are presented in Table 5.

One general observation should also be mentioned. This is a close resemblance between the structures and properties of different complexes. As seen from Table 5, for all complexes their fragments were separated by a distance of about 3.5 Å. The fragment planes were always parallel (the angles $\theta_1 = \theta_2 = \varphi_1 = \varphi_2 = 0$; we did not include the respective figures in Table 5 because of their similarity). Both the total energy U and its components Δ_π and U_V were practically independent of the angle θ_3, so the internal rotation in all complexes could be considered as free. Even the π-electron SE, Δ_π, appeared to be quite weakly sensitive to the nature of the donor component. The latter observation is of particular importance, because it does not agree with the concepts of the simple theory of charge transfer complexes [1]. For instance, one could expect more significant changes in the stability of complexes in the above considered series basing on the values of HOMO energies of the respective donor π-systems. Moreover, the TCNE-anthracene complex does not at all obey the correlation between the stability of a complex and the HOMO energy of its donor component as stated by the simple theory. This lack of the specificity of π-interaction found in the present calculation may be associated with the fact that at a large intermolecular separation all interactions between all π-orbitals of the fragments become very weak and almost equally intensive. The specificity of π-interaction was recovered when it was artificially intensified by shortening the interfragment distance. So we investigated the dependence of Δ_π on the internal rotation angle θ_3 in the TCNE-anthracene system taking $r = 1.5$ Å and observed its change by 46 kcal/mole when θ_3 changed by 90°.

5. Calculation of the Benzene–Carbocyanide Complex

It was of certain interest to compare our calculations with some *ab initio* results. The only object available for such a comparison seemed to be the benzene-carbocyanide complex investigated by Morokuma and co-workers [4, 5]. The geometry of this complex was found by varying a single parameter, the intermolecular distance r, in the framework of the STO-3G calculation. The formation energy, U, was obtained by the 4-31G recalculation for that equilibrium geometry. The following results were obtained: $r = 3.6$ Å, $U = -4.2$ kcal/mole.

In our calculation we used the parameters of the empirical potential (2) presented in Table 4. The parameters for the oxygen atom were accepted to be equal to those of the carbon atom. This simple choice seems appropriate, being in qualitative accordance with the experience of exp-6 calculations of several authors (see for instance Refs. [27, 28]).

The calculated geometry and formation energy of the complex are described by the following values: $r = 3.3$ Å; $\theta_1 = \theta_2 = \varphi_1 = \varphi_2 = 0$; the internal rotation is almost free; $U = -2.5$ kcal/mole. This is in reasonable agreement with the result of the *ab initio* calculation [4, 5]. The latter one neglected electron correlation; on the other hand our method has been calibrated in order to fit the experimental data. That is why it was not at all evident which of the two calculations was more reliable (unfortunately, we were unable to find experimental data on this complex). We tried to achieve better agreement with the *ab initio* calculation by varying the oxygen atom–atom parameters. However, this appeared to be impossible when the variation was kept within reasonable limits.

Appendix: Calculation of the Kinetic Energy Matrix in the Rigid-Fragment Approximation

We use the following notations: 0_1, 0_2 and 0 (see Fig. 1) are the centers of mass (c.m.) of the first fragment, the second fragment and the whole complex, respectively; $\{X_i\}$, $\{Y_i\}$ and $\{Z_i\}$ are the sets of cartesian coordinates fixed in their c.m.; $\{\theta_i\}$, $\{\varphi_i\}$ and $\{\psi_i\}$ are the rotational angles of the first fragment, the second fragment and the whole complex assigned to the axes $\{X_i\}$, $\{Y_i\}$ and $\{Z_i\}$, respectively; N_1 and N_2 are the numbers of atoms in fragments, and $N = N_1 + N_2$ is the number of atoms in a complex; $1 \le \alpha \le N_1$ and $1 \le \beta \le N_2$ are the indices of atoms in the first and second fragments, respectively, and $1 \le \gamma \le N$ are the indices of atoms in a complex, with $\gamma = \alpha$ for the atoms of the first fragment and $\gamma = \beta + N_1$ for the atoms of the second one; m_α, m_β, m_γ – are the masses of atoms; $M_1 = \sum_\alpha m_\alpha$; $M_2 = \sum_\beta m_\beta$ and $M = \sum_\gamma m_\gamma = M_1 + M_2$ are the masses of the first and the second fragments and of the complex; r_1 is the distance 00_1, r_2 is the distance 00_2 and $r = r_1 + r_2$ is the distance O_1O_2.

The condition of the separation of the c.m. translations gives the expressions for r_1 and r_2 in terms of r:

$$r_1 = rM_2/M; \qquad r_2 = rM_1/M. \tag{5}$$

Mass-weighted coordinates $\varkappa^i_\gamma$, η^i_γ and ξ^i_γ are introduced as follows:

$$\begin{aligned} \varkappa^i_\gamma &= m^{1/2}_\gamma x^i_\gamma \\ \eta^i_\gamma &= m^{1/2}_\gamma y^i_\gamma \\ \xi^i_\gamma &= m^{1/2}_\gamma z^i_\gamma \end{aligned} \tag{6}$$

where x^i_γ, y^i_γ and z^i_γ are the coordinates of γth atom in $\{X_i\}$, $\{Y_i\}$ and $\{Z_i\}$, respectively. It is easily seen from Fig. 1 with (5) in mind that the mass-weighted coordinates are related by the following expressions:

$$\begin{aligned} \varkappa^i_\gamma &= \xi^i_\gamma + \delta^i_3 r m^{1/2}_\gamma M_2/M \\ \eta^i_\gamma &= \xi^i_\gamma - \delta^i_3 r m^{1/2}_\gamma M_1/M \\ \varkappa^i_\gamma &= \eta^i_\gamma + \delta^i_3 r m^{1/2}_\gamma \end{aligned} \tag{7}$$

where δ^i_3 is the Kroneker δ^i_j symbol with $j = 3$.

Using the dependence of the mass-weighted coordinates of atoms (6) on the independent coordinates (3) determining the internal geometry and the space orientation of a complex, one can calculate the elements of the kinetic energy matrix $g_{\mu\nu}$ according to the formula [29]:[1]

$$\begin{aligned} g_{\mu\nu} &= \sum_{i,\gamma} \frac{\partial \xi^i_\gamma}{\partial q^\mu} \frac{\partial \xi^i_\gamma}{\partial q^\nu} = \sum_{i,\gamma} \frac{\partial \xi_{i\gamma}}{\partial q^\mu} \frac{\partial \xi_{i\gamma}}{\partial q^\nu} \\ &= \sum_{i,\alpha} \frac{\partial \xi_{i\alpha}}{\partial q^\mu} \frac{\partial \xi_{i\alpha}}{\partial q^\nu} + \sum_{i,\beta} \frac{\partial \xi_{i\beta}}{\partial q^\mu} \frac{\partial \xi_{i\beta}}{\partial q^\nu}. \end{aligned} \tag{8}$$

For that purpose it is sufficient to know the expressions for the derivatives $\partial \xi_{i\gamma}/\partial q^\nu$. Let us first calculate $\partial \xi_{i\gamma}/\partial q^6$, i.e. $\partial \xi_{i\gamma}/\partial r$. Since $\varkappa^i_\alpha$ and η^i_β are independent of r, the differentiation (7) with respect to r gives:

$$\frac{\partial \xi_{i\alpha}}{\partial r} = -\delta_{i3} m^{1/2}_\alpha M_2/M; \qquad \frac{\partial \xi_{i\beta}}{\partial r} = \delta_{i3} m^{1/2}_\beta M_1/M. \tag{9}$$

In order to calculate the derivatives of $\xi_{i\gamma}$ with respect to angular coordinates we use the well known expression for the infinitesimal rotation vector $\mathbf{d\Omega}$ of the point vector $\boldsymbol{n}$:[2]

$$\mathrm{d}n_i = \varepsilon_{kji}\, \mathrm{d}\Omega^k n^j$$

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[1] Mass-weighted coordinates are Cartesian, so their covariant and contravariant components are the same ($\xi^i_\gamma = \xi_{i\gamma}$ etc).

[2] Here and below summation is implied with respect to repeating indices.

where ε_{kji} is the Levi–Chivitta symbol [29]. Then for mass-weighted coordinate ρ_i, we obtain

$$\frac{\partial \rho_i}{\partial \Omega^k} = \varepsilon_{kji}\rho^j.$$

Being applied to the coordinates (6) this gives

$$\begin{aligned}
\frac{\partial \xi_{i\gamma}}{\partial \psi^k} &= \varepsilon_{kji}\xi^j_\gamma \\
\frac{\partial \varkappa_{i\alpha}}{\partial \theta^k} &= \varepsilon_{kji}\varkappa^j_\alpha \\
\frac{\partial \eta_{i\beta}}{\partial \varphi^k} &= \varepsilon_{kji}\eta^j_\beta.
\end{aligned} \tag{10}$$

Since $\varkappa_{i\beta}$ are independent on θ^k, and $\eta_{i\alpha}$ are independent of φ^k, relations (10) can be complemented by

$$\begin{aligned}
\frac{\partial \varkappa_{i\beta}}{\partial \theta^k} &= 0 \\
\frac{\partial \eta_{i\alpha}}{\partial \varphi^k} &= 0.
\end{aligned} \tag{11}$$

And finally, by differentiating (7) with respect to θ^k and φ^k, we get

$$\begin{aligned}
\frac{\partial \xi_{i\gamma}}{\partial \theta^k} &= \frac{\partial \varkappa_{i\gamma}}{\partial \theta^k} \\
\frac{\partial \xi_{i\gamma}}{\partial \varphi^k} &= \frac{\partial \eta_{i\gamma}}{\partial \varphi^k}.
\end{aligned} \tag{12}$$

All necessary information concerning $\partial \xi_{i\gamma}/\partial q^\nu$ is contained in expressions (9)–(12). This allows performing summation (8). Finally we come out with

$$\|g_{\mu\nu}\| = \left[\begin{array}{ccc|cc|c|ccc}
I^{(1)}_{11} & I^{(1)}_{12} & I^{(1)}_{13} & & & & I^{(1)}_{11} & I^{(1)}_{12} & I^{(1)}_{13} \\
I^{(1)}_{21} & I^{(1)}_{22} & I^{(1)}_{23} & & 0 & & I^{(1)}_{21} & I^{(1)}_{22} & I^{(1)}_{23} \\
I^{(1)}_{31} & I^{(1)}_{32} & I^{(1)}_{33} & & & & I^{(1)}_{31} & I^{(1)}_{32} & I^{(1)}_{33} \\
\hline
 & & & I^{(2)}_{11} & I^{(2)}_{12} & & I^{(2)}_{11} & I^{(2)}_{12} & I^{(2)}_{13} \\
 & 0 & & I^{(2)}_{21} & I^{(2)}_{22} & 0 & I^{(2)}_{21} & I^{(2)}_{22} & I^{(2)}_{23} \\
\cline{4-9}
 & & & \multicolumn{2}{c|}{0} & \dfrac{M_1M_2}{M} & \multicolumn{3}{c}{0} \\
\hline
I^{(1)}_{11} & I^{(1)}_{12} & I^{(1)}_{13} & I^{(2)}_{11} & I^{(2)}_{12} & & I_{11} & I_{12} & I_{13} \\
I^{(1)}_{21} & I^{(1)}_{22} & I^{(1)}_{23} & I^{(2)}_{21} & I^{(2)}_{22} & 0 & I_{21} & I_{22} & I_{23} \\
I^{(1)}_{31} & I^{(1)}_{32} & I^{(1)}_{33} & I^{(2)}_{31} & I^{(2)}_{32} & & I_{31} & I_{32} & I_{33}
\end{array}\right]$$

where $I_{ij}^{(1)}$, $I_{ij}^{(2)}$ and I_{ij} are the components of inertia tensors of the 1-st and the 2-nd fragments and the whole complex in $\{X_i\}$, $\{Y_i\}$ and $\{Z_i\}$, respectively:

$$I_{11}^{(1)} = \sum_{\alpha} m_{\alpha}(x_{2\alpha}^2 + x_{3\alpha}^2)$$

$$I_{12}^{(1)} = -\sum_{\alpha} m_{\alpha} x_{1\alpha} x_{2\alpha}$$

$$I_{11}^{(2)} = \sum_{\beta} m_{\beta}(y_{2\beta}^2 + y_{3\beta}^2)$$

$$I_{12}^{(2)} = -\sum_{\beta} m_{\beta} y_{1\beta} y_{2\beta}$$

$$I_{11} = \sum_{\gamma} m_{\gamma}(z_{2\gamma}^2 + z_{3\gamma}^2)$$

$$I_{12} = -\sum_{\gamma} m_{\gamma} z_{1\gamma} z_{2\gamma}.$$

(The other expressions can be obtained by cyclic permutation of the indices 1, 2, 3).

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