# NOTIZEN

## Second Derivatives of the Hartree–Fock–Roothaan Hamiltonian

A. Azman
King's College, Cambridge, England
and Z. Bohte
University of Surrey, London

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In this note we should like to present the second derivatives of the Hartree–Fock–Rothaan Hamiltonian that could be useful in ab-initio calculations of the force constants. We shall use a method similar to that of Rossinkhin and Morozov [1] but extended to polyatomic molecules.

Energy $E$ can be written [2] as

$$E = 2\int [h\,\varrho(q,q')_{q'\to q}]\,\mathrm{d}V + \int r^{-1}[2\,\varrho(q,q)\,\varrho(q',q') - \varrho(q,q')\,\varrho(q',q)]\,\mathrm{d}V\,\mathrm{d}V'$$

with $$\varrho(q,q') = \sum_i \varphi_i(q)\,\varphi_i(q')$$

where $h$ is the one-electron operator and $\varrho$ is the density matrix. Using the fact that $\varphi_i(q)$ form a complete set of eigenfunctions of the Hartree–Fock operator, the first derivatives are easily found as

$$\frac{\partial\varphi_i(q)}{\partial R_n} = \sum_j K^n_{ij}\varphi_j(q)$$

where the matrix $K^n$ is antisymmetric ($K^{n\mathrm{T}} = -K^n$) and $R_n$ is the coordinate. In addition it may be shown that

$$\frac{\partial\varrho(q,q')}{\partial R_n} = 0 \quad \text{and} \quad \frac{\partial^2\varrho(q,q')}{\partial R_n\,\partial R_m} = 0\,.$$

Therefore, the second derivatives of the energy are

$$\frac{\partial R_n\,\partial R_m}{\partial^2 E} = 2\int\left[\frac{\partial^2 h}{\partial R_n\,\partial R_m}\,\varrho(q,q')_{q'\to q}\right]\mathrm{d}V$$

With the Roothaan's approximation [3] $\varphi_i = \sum_p C_{ip}\,\xi_p$ where $\xi_p$ form a complete set of the orthonormalized atomic orbitals, the energy is

$$E = \sum_i\sum_{p,s} C_{ip}(H_{ps}+F_{ps})\,C_{is} = \mathrm{Tr}\,(C(H+F)\,C^{\mathrm{T}}) = \mathrm{Tr}\,(C\,M\,C^{\mathrm{T}})\,.$$

The first derivatives of $E$ are

$$\frac{\partial E}{\partial R_n} = \mathrm{Tr}\left(\frac{\partial C}{\partial R_n}\,M\,C^{\mathrm{T}} + C\,\frac{\partial M}{\partial R_n}\,C^{\mathrm{T}} + C\,M\,\frac{\partial C^{\mathrm{T}}}{\partial R_n}\right).$$

Derivatives of the matrix $C$ can be found using

$$\frac{\partial\varphi_i}{\partial R_n} = \sum_p\left[\frac{\partial C_{ip}}{\partial R_n}\,\xi_p + C_{ip}\,\frac{\partial\xi_p}{\partial R_n}\right] = \sum_{j,p} K^n_{ij}\,C_{jp}\,\xi_p\,.$$

Denoting $$\frac{\partial\xi_p}{\partial R_n} = G^n_{ps}\,\xi_s$$

we obtain $$\frac{\partial C}{\partial R_n} = K^n\,C - C\,G^n.$$

Since the matrices $K^n$ and $G^n$ are antisymmetric we have

$$\frac{\partial E}{\partial R_n} = \mathrm{Tr}\left(C\,\frac{\partial M}{\partial R_n}\,C^{\mathrm{T}}\right)$$

as $\mathrm{Tr}(A\,B - B\,A) = 0$ and $\mathrm{Tr}(C\,A\,C^{\mathrm{T}}) = \mathrm{Tr}\,A$ provided $C^{\mathrm{T}}\,C = 1$. By the same argument we get

$$\frac{\partial^2 E}{\partial R_n\,\partial R_m} = \mathrm{Tr}\left(C\,\frac{\partial^2 M}{\partial R_n\,\partial R_m}\,C^{\mathrm{T}}\right).$$

This expression is, because of using orthonormalized atomic orbitals, simpler as the one derived by Rossinkhin and Morozov for diatomic molecules.

[1] V. V. Rossinkhin and V. P. Morozov, Theor. Eksp. Khim. **4**, 528 [1966]. (Russ.).

[2] R. McWeeny, Rev. Mod. Phys. **32**, 335 [1960].

[3] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 [1951].

## On the Analysis of Triple Correlations in Radiative Capture Reactions

A. A. Kresnin * and V. E. Storizhko *
Atomic Energy Establishment, Cairo, Egypt, U.A.R.

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Attention is given to the advantages of applying a geometry where the primary $\gamma$-quantum is detected in the beam direction in the study of triple angular correlations in radiative capture reactions.

The study of angular correlations is one of the important methods for the determination of spins of excited states and relative contributions of different multipolarities to radiative transitions. In recent years, much attention has been given to the measurement and analysis of triple correlations in radiative capture reactions, since such an analysis results in additional spectroscopic data [1, 2].

* On leave from Physico-Technical Institute, Kharkov, USSR.

[1] A. J. Ferguson, Angular correlation methods in $\gamma$-ray spectroscopy, North-Holland Publishing Company, Amsterdam 1965.

[2] P. B. Smith in Nuclear Reactions, ed. by P. M. Endt and P. B. Smith, North-Holland Publishing Company, Amsterdam 1962, Vol. II.