

NOTIZEN

Second Derivatives of the Hartree-Fock-Roothaan Hamiltonian

A. AZMAN

King's College, Cambridge, England

and Z. BOHTE

University of Surrey, London

(Z. Naturforsch. **22 a**, 1131 [1967]; received 28 April 1967)

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 MOROZOV¹ but extended to polyatomic molecules.

Energy E can be written² as

$$E = 2 \int [h \varrho(q, q') \varrho' \rightarrow q] dV + \int r^{-1} [2 \varrho(q, q) \varrho(q', q') - \varrho(q, q') \varrho(q', q)] dV dV'$$

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

where h is the one-electron operator and ϱ 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

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

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

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

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

Therefore, the second derivatives of the energy are

$$\frac{\partial R_n \partial R_m}{\partial^2 E} = 2 \int \left[\frac{\partial^2 h}{\partial R_n \partial R_m} \varrho(q, q') \varrho' \rightarrow q \right] dV$$

With the ROTHAAAN'S approximation³ $\varphi_i = \sum_p C_{ip} \xi_p$ where ξ_p form a complete set of the orthonormalized atomic orbitals, the energy is

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

The first derivatives of E are

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

Derivatives of the matrix C can be found using

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

Denoting $\frac{\partial \xi_p}{\partial R_n} = G_{ps}^n \xi_s$

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

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

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

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

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

tion 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}.

² P. B. SMITH in Nuclear Reactions, ed. by P. M. ENDT and P. B. SMITH, North-Holland Publishing Company, Amsterdam 1962, Vol. II.

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.

(Z. Naturforsch. **22 a**, 1131—1132 [1967]; received 2 May 1967)

Attention is given to the advantages of applying a geometry where the primary γ -quantum is detected in the beam direc-

* On leave from Physico-Technical Institute, Kharkov, USSR.
¹ A. J. FERGUSON, Angular correlation methods in γ -ray spectroscopy, North-Holland Publishing Company, Amsterdam 1965.



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.