NOTIZEN

Second Derivatives of the Hartree–Fock–Roothaan Hamiltonian

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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

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

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

where h is the one-electron operator and 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 ($K^{n\mathrm{T}} = -K^n$) 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 ξ_p form a complete set of the orthonormalized atomic orbitals, the energy is

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

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

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

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

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

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.

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On the Analysis of Triple Correlations in Radiative Capture Reactions

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Attention is given to the advantages of applying a geometry where the primary γ-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].

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1 A. J. FERGUSON, Angular correlation methods in γ-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.

The theory of triple correlations for the case of isolated resonances has been developed by several authors (l. c. [3, 4]). However, its direct application for the case of overlapping resonances is associated with many difficulties. LITHERLAND and FERGUSON [4] suggested a method of analysis in which the stage of formation of the decaying state in eliminated from consideration. This method considers population parameters of magnetic substates (statistic tensor parameters) describing the alignment of a decaying state as the parameters which are to be determined from the analysis of experimental data. In a general case, the analysis of triple correlations in radiative capture reactions $X(x, \gamma\,\gamma)\,Y$ requires the determination of many parameters and, consequently, measurements for a number of geometries. Usually, the correlations are measured in geometries I, II, VI, VII (the notation of LITHERLAND and FERGUSON [4]) and angular distributions of γ-quanta are measured as well.

The purpose of this letter is to emphasize the advantages of applying the rarely used geometry IV, where the first γ-quantum is detected along the direction of an incident particle beam. In fact, in this case one may apply the method suggested by LITHERLAND and FERGUSON [4] for the analysis of triple correlations in $X(a,b\gamma)\,Y$ reactions.

In the considered case of the $X(x,\gamma\gamma)\,Y$ reactions (Fig. 1) owing to axial symmetry of the problem and

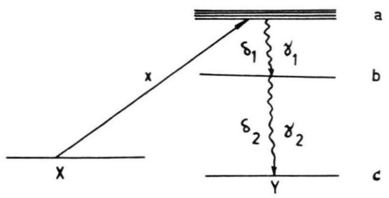

Fig. 1. Energy level diagram showing the notations used.

equality to zero of the projection of orbital momentum on the direction of particle motion, the spin projections on beam direction are related as follows:

$$m_b \leqq m_X + m_x + 1 \tag{1}$$

and the population of magnetic substates is symmetric between positive and negative values. Thus, the analysis of experimental data would require, in the general case, the determination of one mixing parameter and not more than m_b population parameters. In practical cases of proton, neutron or α-particle radiative capture by nuclei with spin 0 or 1/2, the determination of two parameters only (one mixing parameter and one population parameter) would be necessary.

A virtual calculation of angular correlations may be performed using the expression:

$$W(\Theta) = \sum_K \varrho_K(S_b)\, F_K(S_b\, S_Y)\, P_K(\cos\Theta)\, Q_K \tag{2}$$

where Q_K are the attenuation coefficients and where the values for the statistical tensors ϱ_K and F_K-coefficients are tabulated in ref. [5]. Formula (2) may easily be generalized for the case of unobserved intermediate γ-radiations [5].

In the case when the state "a" has a well defined spin and parity, and a mixing parameter δ_1 of the primary γ-radiation is known, the population parameter of the state "b" can be directly determined from the formula:

$$\begin{aligned} P_{m_b}(S_b) = \sum_{m_a+m_b=\pm 1} & P_{m_a}(S_a)\,(1+\delta_1^2)^{-1} \\ & \times [(L_1\, m_a + m_b\, S_b - m_b \mid S_a\, m_a)^2 \\ & + \delta_1^2 (L_1'\, m_a + m_b\, S_b - m_b \mid S_a\, m_a)^2]. \end{aligned} \tag{3}$$

The difference between formula (3) and the analogous one given in ref. [6] is that the summation in (3) is limited by the values $m_a + m_b = \pm 1$ associated with the necessity of taking into acount the γ-quantum transversality in the geometry considered.

The analysis of two available measurements [7, 8] on $(p,\gamma\gamma)$ correlations in geometry IV has given values of the mixing parameters in agreement with those previously obtained.

The described method, apart from its obvious simplicity may readily be applied to practically all the reactions of radiative capture, whereas the use of the method suggested by LITHERLAND and FERGUSON is rather limited. Another attractive feature of the considered method is that the decaying state should not necessarily be a state with well defined spin and parity.

In practice this means that correlation measurements may be performed with thick targets which is important for the investigation of the radiative capture reactions on medium and heavy nuclei, where the level density is high and the reaction cross-sections are small.

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