Note on Calculating Energy Values of Rotationally Hindered Linear Molecules

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The variational principle based on an integral equation equivalent to the Schrödinger equation is employed to calculate energy levels of Devonshire's model.

In the preceding paper*, henceforth cited as I, the Ritz-Galerkin method based on the Schrödinger equation of Devonshire's model was used to calculate the lowest-lying energy states of the rigid dumb-bell in an external field of octahedral symmetry. A similar variational technique was applied to a corresponding integral equation. Energy levels of the symmetry type $T_{2g}$ were evaluated in this way and are compared with results of I to have a test of the effectiveness of the integral equation method. The technique concerned has extensively been exploited for energy band calculations 1 in solid state physics and is known as the Kohn-Rostoker method.

The Schrödinger equation of the system

$$B \cdot \left( \frac{\mathbf{q}^2}{\hbar^2} + V(\mathbf{q}) \right) \psi = B \cdot E \psi,$$

(1)

$V$ being the Devonshire potential

$$-2 \cdot \sqrt{\frac{4\pi}{21}} K X^4_4,$$

is transformed into an integral equation by means of the Green's function

$$G_E(\mathbf{q}, \mathbf{q'}) = \sum_{l,m} \frac{Y^*_{l,m}(\mathbf{q}) Y_{l,m}(\mathbf{q'})}{l(l+1)-E} = \sum_{d,\kappa, l,v} \frac{X^{d\kappa}_{l,v}(\mathbf{q}) X^{d\kappa}_{l,v}(\mathbf{q'})}{l(l+1)-E},$$

(2)

that satisfies

$$\left( \frac{\mathbf{q}^2}{\hbar^2} - E \right) G_E(\mathbf{q}, \mathbf{q'}) = \delta(\mathbf{q}, \mathbf{q'}).$$

(3)

The resulting integral equation

$$\psi(\mathbf{q}) + \int G_E(\mathbf{q}, \mathbf{q'}) V(\mathbf{q'}) d \mathbf{q'} = 0$$

(4)

* The notation used in this paper was taken over from the preceding one.

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can be derived from the variational principle

\[ \delta \left[ \int_0^\infty \varphi(\Omega) V(\Omega) \varphi(\Omega) \, d\Omega + \right. \\
\left. \int_0^\infty \varphi(\Omega) V(\Omega) G_E(\Omega, \Omega') V(\Omega') \varphi(\Omega') \, d\Omega \, d\Omega' \right] = 0. \]  

Expanding the energy eigenfunction \( \varphi \) in terms of the complete set of symmetry-adapted angular momentum eigenfunctions,

\[ \varphi = \sum_{D, \kappa, l, v} c_{l, v}^{D, \kappa} X_{l, v}^{D, \kappa}, \]  

the variational principle (5) yields a determinantal condition for the energy eigenvalues. The determinant is of infinite rank, but it can be factorized with respect to the symmetry type of the energy levels:

\[ \prod_D \det \left( V_{l, v, l', v'} + \sum_{l'', v''} \frac{V_{l, v, l'', v''} V_{l', v', l'', v''}}{l''(l'' + 1) - E} \right) = 0, \]

\[ V_{l, v, l', v'} = \int X_{l, v}^{D, \kappa}(\Omega) V(\Omega) X_{l', v'}^{D, \kappa}(\Omega) \, d\Omega, \]

\( V_{l, v, l', v'} \) being as \( H_{l, \kappa} \) in (5) of \( I \) independent of the row label \( \kappa \), since \( V \) transforms according to the totally symmetric representation \( A_{1g} \) of \( O_h \). If the constituent matrix elements \( V_{l, v, l', v'} \) are not available, the term

\[ \prod_D \det \left( V_{l, v, l', v'} + \sum_{l'', v''} \frac{V_{l, v, l'', v''} V_{l', v', l'', v''}}{l''(l'' + 1) - E} \right) = 0, \]

in (7) can be calculated by means of the first form of the Green’s function in (2),

\[ \sum_{l', v'} V_{l, v, l', v'}^{D} = \int_{l, v} X_{l, v}^{D, \kappa}(\Omega) V(\Omega) Y_{l', m}(\Omega) Y_{l', m}(\Omega') V(\Omega') X_{l', v'}^{D, \kappa}(\Omega') \, d\Omega \, d\Omega'. \]

Performing the same approximation for the energy eigenfunction as in I, i.e. replacing (6) by a finite series expansion,

\[ \varphi = \sum_{l=0}^{12} \sum_{D, \kappa, v} c_{l, v}^{D, \kappa} X_{l, v}^{D, \kappa}, \]

that takes angular momentum quantum numbers \( l \) up to 12 only into account, condition (7) is truncated to a product of finite determinants, each one allowing approximate solutions for the lowest energy eigenvalues of a definite symmetry type. Though the factorization of the determinant saves immense computational work, much effort still is