TRANSFORMATION OF QUANTUM MECHANICAL OPERATOR MATRIX FROM CARTESIAN TO CYLINDRICAL NORMAL COORDINATES IN QUASI-DIABATIC BASIS

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As described in the previous talk, if one is analyzing a spectrum involving rotational and fine structure, the cylindrical representation of the potential energy matrix in the quasi-diabatic basis, $\mathbf{V_{cyl}}$, is more convenient due to the simple form of rovibronic Hamiltonian. It also facilitates the identification of the symmetry of the vibronic basis functions.[a] On the other hand, *ab initio* parameterization of the vibronic Hamiltonian is typically performed in the Cartesian representation, $\mathbf{V_{cart}}$. The two matrix representations for a molecule with a simple, linear Jahn–Teller $E \times e$ effect can be written as

$$\mathbf{V_{cyl}} = \begin{bmatrix} \frac{1}{2}\omega Q_+ Q_- & kQ_+ \\ kQ_- & \frac{1}{2}\omega Q_+ Q_- \end{bmatrix} \qquad \mathbf{V_{cart}} = \begin{bmatrix} \frac{1}{2}\omega(Q_a^2 + Q_b^2) + kQ_a & -kQ_b \\ -kQ_b & \frac{1}{2}\omega(Q_a^2 + Q_b^2) - kQ_a \end{bmatrix}$$

where $Q_\pm = Q_a \pm iQ_b$ are the normal modes. Here the corresponding electronic basis sets are related as $\Phi_\pm = \frac{1}{\sqrt{2}}(\Phi_a \pm i\Phi_b)$. Transforming $\mathbf{V_{cart}}$ into $\mathbf{V_{cyl}}$ through coordinate substitution together with the basis set transformation becomes tedious for higher-order expansions, especially considering multimode and multistate problems. It is therefore desirable to develop a general procedure that can be used for the transformation of operators from the Cartesian form to the cylindrical one.

In this talk, we will show that the potential energy operator represented in a tensor form can be naturally transformed from Cartesian to cylindrical representation through a series of tensor-matrix multiplications, provided that the two matrices transforming the vibrational normal coordinates and the electronic basis set are known. In general, this method can be used to transform any quantum mechanical operator matrix.

We demonstrate the effectiveness of this method with calculations for NO_3 and CH_3O.

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[a] Bunker, P.R., and Jensen, P. 2006. Molecular symmetry and spectroscopy. 2nd ed. NRC Research Press, Ottawa, Canada, p. 290 ff.