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Ajit Banerjee, James O. Jensen, and Jack Simons

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Translation-rotation invariance for N-particle systems: Internal coordinates and search for stationary points in reduced spaces

Ajit Banerjee, James O. Jensen, and Jack Simons
Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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Using the translational and rotational invariance of the energy, we show that for an N-body system there exists a subset of $3N-6$ Cartesian coordinates such that the derivatives of the energy of a given order with respect to the members of this subset form an independent and complete set. That is, all other derivatives can be calculated knowing these independent derivatives. We further show that this subset of coordinates can be chosen to be a bonafide set of internal coordinates. Since these coordinates are a subset of the $3N$ Cartesian coordinates, they are orthonormal and uniform. Applications have been made of such internal coordinates in algorithms which search for stationary points on potential energy surfaces. It is shown that the surface walking algorithms are exactly separable for these coordinates. Thus the problem can be reexpressed in terms of $(3N-6)$ Cartesian variables without the annoying zero eigenvalues of the Hessian (of the energy) matrix corresponding to the translational and rotational eigenvalues.

I. INTRODUCTION

Ab initio potential energy derivatives are beginning to be progressively useful for providing quantitative descriptions of chemical systems in areas such as molecular structure determination, molecular dynamics, vibrational spectroscopy, and statistical mechanics.[1-5] For N particles the total energy and its derivatives are often generated in terms of $3N$ space fixed coordinates (usually Cartesian coordinates).[6] Displacements along all such $3N$ directions involve components of overall translation and rotation of the system. The energy remains invariant to translations and rotations, and thus components of translation and rotation are unnecessary and undesirable. Furthermore, when dealing with potential energy surfaces, the zero eigenvalues of the Hessian corresponding to translation and rotation are hard to distinguish from near zero (low frequency) eigenvalues of the internal degrees of freedom.

The subject of internal coordinates has been dealt with for a long time.[2,7-10] For those properties of a system that are invariant under translation and rotation, our aim is to find a set of $(3N-6)$ coordinates in which these properties are completely determined and in which the "equations of motion"are separable. Here the "equation of motion" stands, e.g., for classical or quantum mechanical equations of motion, or surface walking algorithms.[11,12] The oldest among these coordinate systems is the so-called Jacobi coordinates[8] with the three translational coordinates being those of the center of mass (c.m.) and the remaining $(3N-3)$ coordinates being relative to the c.m. A commonly used choice of internal coordinates[2] for N particles is to choose, for an arbitrary indexing of the particles, $N-1$ relative distances R_{ij} $(i<j)$, $N-2$ in-plane angles between sets of triples (ijk), and $N-3$ dihedral angles between these planes. Such coordinates have been widely used for treating small vibrations around equilibrium geometries.[2] Thomas and Emerson[13] have used the c.m. translation with (infinitesimal) rotational invariance conditions (Eckart coordinates[14]) as constraints for a Newton–Raphson surface walking algorithm through the use of Lagrange multipliers. The walking algorithm thus yields step vectors which remain orthogonal to the eigenvectors of the translation and infinitesimal rotation.

We focus our attention in this paper on the considerations of translational and rotational symmetries for the energy of N-particle systems. Here we show that there exists a subset of $(3N-6)$ Cartesian coordinates such that the derivatives of the energy to any given order with respect to coordinates of this subset form an independent and complete set. That is, all other derivatives can be calculated knowing these independent derivatives. We further show that this subset can be chosen to be a bonafide set of internal coordinates. We then apply these ideas toward searches for stationary points on potential energy surfaces in a $(3N-6)$-dimensional subspace. The resulting steps are devoid of *any* components of overall translation or rotation of *any* order. The Cartesian nature of these internal coordinates have the benefits of orthogonality and uniformity. In what follows, we choose the invariant property of the system to be the energy since most equations of motion are written in terms of some form of energy. However, the development presented here is applicable to any other invariant property.

II. TRANSLATIONAL AND ROTATIONAL SYMMETRY OF ENERGY

The main idea developed in this section is that, due to the invariance of the total energy under overall translation and rotation of an N-body system, there exists certain relationships among the derivatives of the energy relative to the $3N$ Cartesian coordinates. That is, not all derivatives of energy of a given order are independent. For example, for a two-particle system, a consequence of translational invariance is that $\partial E/\partial P_{1\alpha} = -\partial E/\partial P_{2\alpha}$ $(\alpha = x, y, z)$ where $P_{K\alpha}$ refers to the αth Cartesian coordinate of the K th particle. More

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specifically, we will show in this section that there exists a subset of $3N-6$ ($3N-5$ for linear geometries) Cartesian coordinates such that all unique derivatives of a given order constructed with respect to these coordinates form an independent and complete set.

We start by obtaining a representation of the translation $\hat{T}$ and rotation $\hat{R}$ operators. We note that the action of the $\hat{T}$ or $\hat{R}$ operator is to translate or rotate (about an axis taken here to be passing through the lab fixed origin) all points $\mathbf{P}_K$ in space. The energy depends directly upon the $\{\mathbf{P}_K\}$.

For the case of quantum mechanical potential energy within the Born–Oppenheimer separation where the contributions due to the motion of electrons have been integrated over, the rotation of all nuclear centers $\mathbf{P}_K$ is assumed to mean that the associated electron distributions are also correspondingly rotated. The total energy and its derivatives remain invariant under $\hat{T}$ and $\hat{R}$:

$$E(\{\mathbf{P}_K\}) = E(\hat{T}\{\mathbf{P}_K\}), \tag{1}$$

$$E(\{\mathbf{P}_K\}) = E(\hat{R}\{\mathbf{P}_K\}). \tag{2}$$

Equations (1) and (2) also hold when E is replaced by a first derivative $\partial E/\partial P_{K\alpha}$, or by a second derivative $\partial^2 E/\partial P_{K\alpha}\,\partial P_{J\beta}$, or higher order derivatives.

The operator $\hat{T}$ that induces a translation of all points $\mathbf{P}_K$ by a vector $t=(t_x,t_y,t_z)$ can be represented as

$$\hat{T} = \exp\left\{\mathbf{t}\cdot\sum_K \nabla_{P_K}\right\}, \tag{3}$$

where $\nabla_{P_K} = (\partial/\partial P_{Kx}, \partial/\partial P_{Ky}, \partial/\partial P_{Kz})$ defines the gradient operator at the point $\mathbf{P}_K$. Similarly, the operator $\hat{R}$ which generates rotation of all points by an angle $\phi=(\phi_x,\phi_y,\phi_z)$ about an axis along the direction $\boldsymbol{\phi}$ through the lab-fixed origin is

$$\hat{R} = \exp\left\{\boldsymbol{\phi}\cdot\sum_K \mathbf{L}_K\right\}, \tag{4a}$$

where

$$\mathbf{L}_K = \mathbf{P}_K \times \nabla_{P_K}. \tag{4b}$$

The operators $\mathbf{L}_K$ of course satisfy the usual commutation relations

$$[L_{K\alpha}, L_{J\beta}] = -\delta_{KJ}\, L_{K\gamma}, \quad \alpha\beta\gamma = xyz, yzx, zxy.$$

A. Invariance relations for energy derivatives

Here we rewrite the invariance relations of Eqs. (1) and (2) in the representations of $\hat{T}$ and $\hat{R}$, given in Eqs. (3) and (4), respectively, for all orders in t and ϕ. The resulting equations for each order in t and ϕ yield relations among the derivatives of the energy from which an independent set of derivatives of each order can be constructed. Given this set of independent derivatives, the dependent derivatives can be directly obtained from the above relations. In earlier publications[15,16] we have undertaken a similar analysis of the invariance relations for quantum mechanical integrals. Here we shall only stress the main points, starting with the translational invariance. Expanding Eq. (1) for E in a Taylor series, we have

$$E = E + \sum_{\alpha=x,y,z} t_\alpha \sum_{K=1}^{N} E_{K\alpha} + \frac{1}{2!} t_\alpha\, t_\beta \sum_{KJ}^{N} E_{K\alpha J\beta} + \frac{1}{3!}\sum_{\alpha\beta\gamma} t_\alpha\, t_\beta\, t_\gamma \sum_{KJM}^{N} E_{K\alpha J\beta M\gamma} + \cdots, \tag{5}$$

where the shorthand notation

$$E_{K\alpha} = \frac{\partial E}{\partial P_{K\alpha}}, \quad E_{K\alpha J\beta} = \frac{\partial^2 E}{\partial P_{K\alpha}\,\partial P_{J\beta}}, \quad \text{etc.}$$

has been introduced. Since the t_α are independent and can be chosen to be of arbitrary magnitudes, terms of each order in t must separately vanish. Furthermore, an expansion similar to Eq. (5) holds for the invariance of the first derivatives $E_{J\beta}$ for the second derivatives $E_{J\beta M\gamma}$, and so on. Then the vanishing first order terms give

$$\hat{T}^{(1)} E \equiv \sum_{K=1}^{N} E_{K\alpha} = 0, \quad \alpha = x,y,z. \tag{6}$$

These are the three relations among the gradients of energy. There are however two ways to generate relations among the Hessians of energy. From the invariance of energy of Eq. (5) one obtains

$$\hat{T}^{(2)} E = \sum_{KJ}^{N} E_{K\alpha J\beta} = 0, \quad \alpha\beta = \begin{matrix} xx, yy, zz, \\ xy, yz, zx \end{matrix}$$

and from the invariance of the derivatives $E_{J\beta}$ one obtains

$$\hat{T}^{(1)} E_{J\beta} = \sum_{K=1}^{N} E_{K\alpha J\beta} = 0, \quad \alpha,\beta = x,y,z; \quad J = 1,N. \tag{7}$$

The six relations of $\hat{T}^{(2)} E$ can be constructed from the $9N$ relations of Eq. (7) by summing over J. The $9N$ independent relations of Eq. (7) constitute the constraints on the Hessian elements. Similarly, for the third derivatives among the relations $\hat{T}^{(3)} E$, $\hat{T}^{(2)} E_{M\gamma}$, and $\hat{T}^{(1)} E_{J\beta M\gamma}$, the first two relations can be constructed from the latter, where

$$\hat{T}^{(1)} E_{J\beta M\gamma} \equiv \sum_{K=1}^{N} E_{K\alpha J\beta M\gamma} = 0, \quad \begin{matrix} \alpha,\beta,\gamma = x,y,z, \\ J,M = 1,N \end{matrix}. \tag{8}$$

In general, a complete set of translational invariance relations of nth order can be written as $\hat{T}^{(1)} E^{(n-1)} = 0$, where $E^{(n-1)}$ refers to the set of all $(n-1)$th derivatives of energy.

Obtaining relations for the rotational invariance for each order follows exactly along the same lines. One writes the expansion of Eq. (2) [similar to that of Eq. (5)] for E and its derivatives $E_{J\beta}$, $E_{J\beta M\gamma}$,$\cdots$. Then terms of each order of the expansion yield relations among derivatives of energy. Similar to the case of translational invariance, a complete set of rotational invariance relations for the nth order derivatives of E can be written as $\hat{R}^{(1)} E^{(n-1)} = 0$. Using definition of $\hat{R}^{(1)} \equiv \Sigma_{K=1}^{N} \mathbf{L}_K$ and Eq. (4b), the first three of these relations can be written explicitly as

$$\sum_{K=1}^{N} \{P_{K\alpha} E_{K\beta} - P_{K\beta} E_{K\alpha}\} = 0, \tag{9}$$

$$\sum_{K=1}^{N} \{P_{K\alpha} E_{K\beta J\mu} - P_{K\beta} E_{K\alpha J\mu}\} = 0, \quad \begin{matrix} \alpha\beta = xy, yz, xz, \\ \mu,\nu = x,y,z, \\ J,M = 1,N, \end{matrix} \tag{10}$$

and

$$\sum_{K=1}^{N} \{ P_{K\alpha} E_{K\beta J\mu M\nu} - P_{K\beta} E_{K\alpha J\mu M\nu} \} = 0, \quad (J\mu) \leqslant (M\nu). \tag{11}$$

III. INDEPENDENT ENERGY DERIVATIVES

So far we have obtained relationships among the derivatives of the energy $E_{K\alpha}, E_{K\alpha J\beta}, \ldots$, based on their translational and rotational invariance. Our aim next is to find, from the relationships, sets of independent (and dependent) derivatives of the energy of a given order. Toward this goal, we note that the relationships given in Eqs. (6)–(8) and Eqs. (9)–(11), for a given order in the energy derivative, constitute a system of m simultaneous homogeneous linear equations with n energy derivatives as the variables. The coefficient matrix $(m \times n)$ depends only upon the location of centers $\{\mathbf{P}_K\}$. The problem is to first reduce the respective system of linear equations to one containing only r $(\leqslant m)$ independent relations, where r is the rank of the system of equations, by casting the equations into lower row echelon form.[17] Then one can write r dependent energy derivatives in terms of $n - r$ independent ones. In the following subsections we undertake this task; the case of first derivatives is shown in detail.

A. First derivatives (gradients) of E

For the gradient of energy the relevant relations are given in Eqs. (6) and (9). Toward finding an independent set of gradients, we first simplify by solving Eq. (6) for $E_{1\alpha}$ as

$$E_{1\alpha} = -\sum_{K=2}^{N} E_{K\alpha}, \quad \alpha = x, y, z. \tag{12}$$

Then we eliminate from Eq. (9) the elements $E_{1\alpha}$, to obtain

$$\sum_{K=2}^{N} \{ \hat{P}_{K\alpha} E_{K\beta} - \hat{P}_{K\beta} E_{K\alpha} \} = 0, \quad \alpha\beta = xy, yz, zx, \tag{13}$$

where

$$\hat{P}_{K\alpha} = P_{K\alpha} - P_{1\alpha}, \quad K = 2,N. \tag{14}$$

Since in the new coordinates defined by Eq. (14) the rotational relations of Eq. (13) do not involve $E_{1\alpha}$, they can be solved independently of Eq. (12). Furthermore, Eq. (12) shows that the three derivatives $E_{1\alpha}$ $(\alpha = x, y, z)$ are dependent and can be obtained from $E_{K\alpha}$ $(K = 2,N)$. The remaining set of dependent derivatives are to be found from Eq. (13). Geometrically, the separation obtained here through the coordinate transformation of Eq. (14) is equivalent to translating the origin of lab-fixed coordinate system onto particle 1.

The solution of Eq. (13) for the determination of dependent and independent gradients through its reduction to a lower row echelon form has to be performed as shown in Ref. 15. Here we will merely state the results. First for the special case of a three-particle system Eq. (13) has the form

$$\begin{bmatrix} -\hat{P}_{2y} & \hat{P}_{2x} & 0 & -\hat{P}_{3y} & \hat{P}_{3x} & 0 \\ 0 & -\hat{P}_{2z} & \hat{P}_{2y} & 0 & -\hat{P}_{3z} & \hat{P}_{3y} \\ \hat{P}_{2z} & 0 & -\hat{P}_{2x} & \hat{P}_{3z} & 0 & -\hat{P}_{3x} \end{bmatrix} \begin{bmatrix} E_{2x} \\ E_{2y} \\ E_{2z} \\ E_{3x} \\ E_{3y} \\ E_{3z} \end{bmatrix} = 0. \tag{15}$$

Assuming $\hat{P}_{2y} \neq 0$, from the lower row echelon form of Eq. (15), a particular choice of dependent gradient elements is E_{2x}, E_{2z}, E_{3x} for which the independent elements are E_{2y}, E_{3y}, E_{3z}. Then Eq. (15) can be rewritten as

$$\mathsf{A} \begin{bmatrix} E_{2x} \\ E_{2z} \\ E_{3x} \end{bmatrix} = -\mathsf{B} \begin{bmatrix} E_{2y} \\ E_{3y} \\ E_{3z} \end{bmatrix}, \tag{16}$$

where $\mathsf{A}(3 \times 3)$ is a nonsingular matrix containing the columns 1,3,4 of the coefficient matrix of Eq. (15) corresponding to the variables E_{2x}, E_{2z}, and E_{3x}. Similarly the columns of $\mathsf{B}(3 \times 3N - 6)$ correspond to variables E_{2y}, E_{3y}, and E_{3z}. The generalization of this result for the N-center noncollinear case is that, for $\hat{P}_{2y} \neq 0$, an independent set of $(3N - 6)$ gradient elements can be chosen to be $E_{2y}, E_{3y}, E_{3z}, E_{K\alpha}$ $(K = 4,N;\ \alpha = x, y, z)$. The remaining six dependent gradients $E_{1x}, E_{1y}, E_{1z}, E_{2x}, E_{2z}, E_{3x}$ are obtained from invariance relations; the first three are obtained from Eq. (12) and the last three from Eq. (16).

The case of collinear geometry of the N centers must be treated separately. Due to the diminished geometrical flexibility only two of the three relations of Eq. (13) are independent. For $P_{2y} \neq 0$, the two chosen relations are

$$\sum_{K=2}^{N} \{ \hat{P}_{K\alpha} E_{K\beta} - \hat{P}_{K\beta} E_{K\alpha} \} = 0, \quad \alpha\beta = xy, yz. \tag{17}$$

To deal with collinear geometries one must use Eq. (17) instead of Eq. (13), along with Eq. (12). The result, using the echelon form analysis, is that, for $P_{2y} \neq 0$, an independent set of $(3N - 5)$ gradient elements are $E_{2y}, E_{K\alpha}$ $(K = 3,N;\ \alpha = x, y, z)$. The five dependent gradients are $E_{1x}, E_{1y}, E_{1z}, E_{2x}, E_{2z}$; the first three are obtained from Eq. (12) and the last two from Eq. (17).

B. Second and higher derivatives of E

These results can be generalized for the second derivatives (Hessian) of the energy as well as to higher derivatives

due to the similarity in the form of the invariance relations. As shown in Sec. I, the invariance relations involving the nth derivative of the energy arise from $\hat{T}^{(1)}E^{(n-1)}=0$ and $\hat{R}^{(1)}E^{(n-1)}=0$. In particular, for the second derivatives of the energy the translation and rotation relations, analogous to Eqs. (12) and (13), are

$$E_{1\alpha J\mu} = -\sum_{K=2}^{N} E_{K\alpha J\mu}, \quad \begin{matrix} J=2,N, \\ \alpha,\mu = x,y,z, \end{matrix}$$
$$\sum_{K=1}^{N} E_{1\mu K\alpha} = 0, \quad \alpha,\mu = xx, yy, zz, xy, yz, zx \tag{18}$$

which separate the references of center 1 from the rotational relations

$$\sum_{K=2}^{N} (\hat{P}_{K\alpha} E_{K\beta J\mu} - \hat{P}_{K\beta} E_{K\alpha J\mu}) = 0, \quad \begin{matrix} \alpha\beta = xy, yz, zx, \\ \mu = x,y,z, \\ J=2,N, \\ (S_{xy2z}, S_{zx2x}, S_{zx2z}). \end{matrix} \tag{19}$$

Here $(S_{xy2z}, S_{zx2x}, S_{zx2z})$ represent redundant conditions that must be discarded, where $S_{\alpha\beta J\mu}$ denotes Eq. (19) for given values of α, β, J, and μ. The echelon form of Eq. (19) shows that for $\hat{P}_{2y}\neq 0$ and $\hat{P}_{2y}\hat{P}_{3z}-\hat{P}_{2z}\hat{P}_{3y}\neq 0$, $N'(N'+1)/2$ $(N'=3N-6)$ independent Hessian elements can be constructed from unique combinations of the N' differential elements $\partial P_{2y}, \partial P_{3y}, \partial P_{3z}, \partial P_{K\alpha}$ $(K=4,N;\ \alpha=x,y,z)$. The remaining $[3N(3N+1)/2 - N'(N'+1)/2]$ dependent Hessian elements can be obtained from Eqs. (18) and (19). Comparing this result with the previous result for gradient elements, one finds that it is the *same* $(3N-6)$ differential elements that the *independent* gradient elements are constructed from.

These results assume $\hat{P}_{2y}\neq 0$; similar results are obtained for an arbitrary K, for $P_{K\alpha}\neq 0$, by appropriate permutation of indices. Thus the assumptions $P_{2y}\neq 0$ and $P_{2y}\hat{P}_{3z}-\hat{P}_{2z}\hat{P}_{3y}\neq 0$ are *not* restrictions on the possible geometries of the molecule. The implications of these relations are that the centers 1, 2, and 3 should be chosen such that they do not reside on a line and the axes x, y, and z should be chosen that the y components of centers 1 and 2 are not equal.

Similarly the relations obtained for the Hessians corresponding to the linear geometry for $\hat{P}_{2y}\neq 0$, are

$$\sum_{K=2}^{N} (\hat{P}_{K\alpha} E_{K\beta J\mu} - \hat{P}_{K\beta} E_{K\alpha J\mu}) = 0, \quad \begin{matrix} \alpha\beta = xy, yz, \\ \mu = x,y,z; J=2,N, \\ (S_{xy2z}). \end{matrix} \tag{20}$$

The echelon form of Eq. (20) shows that, for $\hat{P}_{2y}\neq 0$, $N''(N''+1)/2$ $(N''=3N-5)$ independent Hessian elements can be constructed from unique combinations of the $(3N-5)$ differential elements $\partial P_{2y}, \partial P_{K\alpha}$ $(K=3,N;\ \alpha=x,y,z)$. Again, the same differential elements are used to create independent gradient elements for linear geometry.

Similar analysis can be extended to derivatives of energy of an arbitrary order n. Then for nonlinear geometries $N'(N'+1)(N'+2)\ldots(N'+n-1)/n!$ independent nth order derivatives $(N'=3N-6)$ can be constructed from all unique combinations of the $(3N-6)$ differential elements $\partial P_{2y}, \partial P_{3y}, \partial P_{3z}, \partial P_{K\alpha}$ $(K=4,N;\ \alpha=x,y,z)$. For linear geometries, $N'=3N-5$, and the $(3N-5)$ differential elements are $\partial P_{2y}, \partial P_{K\alpha}$ $(K=3,N;\ \alpha=x,y,z)$. These results assume $\hat{P}_{2y}\neq 0$; similar results are obtained for an arbitrary K, for $\hat{P}_{K\alpha}\neq 0$, by appropriate permutation of indices.

IV. CONSTRUCTION OF INTERNAL COORDINATES

We are now ready to use the results of the previous section to construct a set of $3N-6$ ($3N-5$ for collinear system) internal coordinates $\{P_i\}$ for systems or properties of N-body systems which remain invariant relative to overall translation and rotation. The internal coordinates P_i must be such that the set $\{P_i\}$ is independent and complete, and that for *all* orders n, the set of all derivatives of the energy with respect to this set also must be independent and complete. The first criterion allows one to span all geometries of an N-body system which are reachable by $3N$ coordinates. The second criterion allows joining two arbitrary points within the $(3N-6)$-dimensional subspace of internal coordinates.

To arrive at such internal coordinates we begin by writing the energy $E\{P_{K\alpha}\}$ $(K=1,N;\ \alpha=x,y,z)$ explicitly as a function of $3N$ Cartesian coordinates, and then find *only* those coordinates that participate independently in producing change in energy (dE, d^2E, etc.). First the consequence of translational symmetry is

$$dE = \sum_{\alpha=x,y,z}\sum_{K=1}^{N} E_{K\alpha}\, dP_{K\alpha}$$
$$= \sum_{\alpha=x,y,z} \{E_{1\alpha}\, dP_{1\alpha} + \sum_{K=2}^{N} E_{K\alpha}\, dP_{K\alpha}\}. \tag{21}$$

Then using the translational invariance condition of Eq. (12), we have

$$dE = \sum_{\alpha}\sum_{K=2}^{N} E_{K\alpha}\, d(P_{K\alpha} - P_{1\alpha}). \tag{22}$$

This shows that changes in energy depend upon at most $3N-3$ relative variables $\hat{P}_{K\alpha}=P_{K\alpha}-P_{1\alpha}$ $(K=2,N)$, and it does not directly depend upon $P_{1\alpha}(=P_{1\alpha})$. A convenient choice of the variable $P_{1\alpha}$ is to choose it to be a constant, then $dP_{1\alpha}=0$, and $\hat{P}_{K\alpha}$ and $P_{K\alpha}$ differ by a constant. In particular, one may choose $P_{1\alpha}=0$ which amounts to translating the origin onto particle 1 and *remaining* on it for all geometries. Higher order changes in energy show again that the active variables are $\hat{P}_{K\alpha}$ $(K=2,N)$. For example,

$$d^2E = \frac{1}{2}\sum_{\alpha\beta}\sum_{K,J=2}^{N} E_{K\alpha J\beta}\, d\hat{P}_{K\alpha}\, d\hat{P}_{J\beta}. \tag{23}$$

Having eliminated the coordinates of particle 1 as a consequence of translational symmetry, we can now consider consequences of rotational invariance on dE, d^2E, etc. involving coordinates of $N-1$ particles. To simplify writing let $\mathbf{P}=\{P_{2y}, P_{3y}, P_{3z}, P_{K\alpha}\ (K=4,N;\ \alpha=x,y,z)\}^+$, a $3N-6$ dimensional vector, and $\mathbf{Q}=\{P_{2x}, P_{2z}, P_{3x}\}^+$, a three-dimensional vector. Vectors $\mathbf{G}$ and $\mathbf{g}$, respectively, contain the gradient elements relative to $\mathbf{P}$ and $\mathbf{Q}$. Then

$$dE = \sum_{\alpha}\sum_{K=2}^{N} E_{K\alpha}\, dP_{K\alpha}$$
$$= \mathbf{G}^+ d\mathbf{P} + \mathbf{g}^+ d\mathbf{Q}. \tag{24}$$

The gradient elements $\mathbf{g}$ can be written in terms of $\mathbf{G}$ from Eq. (16) as

$$\mathbf{g} = \mathsf{C}\mathbf{G}. \tag{25}$$

Here $\mathsf{C} = -\mathsf{A}^{-1}\mathsf{B}$ where A and B are generalizations of the matrices defined in Eq. (16). Then

$$dE = \mathbf{G}^{+}(d\mathbf{P} + \mathsf{C}^{+} d\mathbf{Q}). \tag{26}$$

This shows that dE depends only upon $(3N-6)$ [$(3N-5)$ for the linear case] relative variables $\mathbf{P} \equiv \mathbf{P} + \mathsf{C}^{+}\mathbf{Q}$. Note that $\mathsf{C}^{+}\mathbf{Q}$ has dimensions of $(3N-6)\times 1$ [$(3N-5)\times 1$ for the linear case], same as that of $\mathbf{P}$, and the C matrix is determined solely by the geometry of the system. A very convenient choice is to have the variables $\mathbf{Q} = \text{constant} = 0$ for which $d\mathbf{Q} = 0$. For the nonlinear case we then have

$$\begin{aligned} dE &= \mathbf{G}^{+} d\mathbf{P} \\ &= E_{2y}\, dP_{2y} + E_{3y}\, dP_{3y} + E_{3z}\, dP_{3z} \\ &\quad + \sum_{\alpha = x,y,z} \sum_{K=4}^{N} E_{K\alpha}\, dP_{K\alpha}. \end{aligned} \tag{27}$$

Higher order changes in E show again that the active variables are $\mathbf{P}$; for example the second-order change, with $\mathbf{Q} = d\mathbf{Q} = 0$, we have

$$d^2E = (d\mathbf{P})^{+}\mathsf{H}\, d\mathbf{P}, \tag{28}$$

where H is a matrix of Hessian elements relative to $(3N-6)$ variables $\mathbf{P}$.

We have shown, so far, that in a translated coordinate system in which the coordinate origin is fixed on particle 1 (i.e., $P_{1\alpha} = dP_{1\alpha} = 0$; $\alpha = x, y, z$) which is then rotated to have particle 2 on the y axis and particle 3 remaining in the yz plane (i.e., $P_{2x} = P_{2z} = P_{3x} = dP_{2x} = dP_{2z} = dP_{3x} = 0$) that the $(3N-6)$ Cartesian coordinates $\mathbf{P} = \{P_{2y}, P_{3y}, P_{3z}, P_{K\alpha}\ (K = 4, N; \alpha = x, y, z)\}^{+}$ are indeed internal coordinates.

In practice, one further requires that a particular equation of motion of interest be separable between the internal coordinates $\mathbf{P} = \{P_{2y}, P_{3y}, P_{3z}, P_{K\alpha}\ (K = 4, N; \alpha = x, y, z)\}$ and the external coordinates $\mathbf{Q} = \{P_{1x}, P_{1y}, P_{1z}, P_{2x}, P_{2z}, P_{3x}\}$. To achieve separability for a specific case, appropriate linear combinations among these coordinates would be necessary. In what follows we show that the "surface walking" algorithms are natually separable among the $\mathbf{P}$ and $\mathbf{Q}$ coordinates. Here, one simply chooses to fix particle 1 to be the origin, particle 2 on the y axis, and 3 on the yz plane, while the movement of the remaining coordinates $\mathbf{P}$ are devoid of the components of the overall translation and rotation of the N-particle system.

A similar analysis for the linear case shows that $\mathbf{P} = \{P_{2y}, P_{K\alpha}\ (K = 3, N; \alpha = x, y, z)\}$ are the internal coordinates. By analogy to the nonlinear case, particle 1 would remain at the origin and particle 2 would remain on the y axis. Translational and rotational symmetry would say nothing about particle 3. However, in this case the molecule has cylindrical symmetry (all centers are on the y axis). Thus the motion of center three in any direction perpendicular to the y axis is equivalent. Therefore, nothing is lost in retraining center three to move in the yz plane, and the final procedure is the same as the nonlinear case.

Before leaving this section, it is instructive to investigate the derivatives of E with the six external variables, i.e., $\partial E/\partial P_{1\alpha}$ in the translated coordinate system and $\partial E/\partial P_{2x}$, $\partial E/\partial P_{2z}$, $\partial E/\partial P_{3x}$ in the rotated system. The coordinate transformation to impose translational symmetry is

$$\hat{P}_{1\alpha} = P_{1\alpha} \tag{29a}$$

and

$$\hat{P}_{K\alpha} = P_{K\alpha} - P_{1\alpha}, \quad K = 2, N. \tag{29b}$$

Here the $\hat{P}_{1\alpha}$ gives the vector for translating the origin while $\hat{P}_{K\alpha}$ (K = 2, N) are defined relative to the translated origin. Using this transformation and invariance Eq. (12), we have

$$\begin{aligned} \partial E/\partial \hat{P}_{1\alpha} &= \sum_{J=1}^{N} (\partial E/\partial P_{J\alpha})(\partial P_{J\alpha}/\partial \hat{P}_{1\alpha}) \\ &= \sum_{J=1}^{N} (\partial E/\partial P_{J\alpha}) = 0, \end{aligned} \tag{30a}$$

$$\partial E/\partial \hat{P}_{K\alpha} = \sum_{J=1}^{N} (\partial E/\partial P_{J\alpha})(\partial P_{J\alpha}/\partial \hat{P}_{K\alpha}) = \partial E/\partial P_{K\alpha}, \quad K = 2, N, \tag{30b}$$

where we have inverted Eq. (29) and used the chain rule. That is, derivatives relative to the external coordinates *vanish* in the translated coordinate system while the derivatives with respect to the relative internal coordinates remain the *same*. Similarly using the second-order translational invariance Eq. (7), one obtains $\partial^2 E/\partial \hat{P}_{1\alpha}\, \partial \hat{P}_{1\beta} = 0$, and similarly for all orders. We note that transformation of Eq. (29) is not unitary, leading to a nonorthogonal system of coordinates. However, having separated the coordinates of particle 1, the transformation of Eq. (29b) for $(N-1)$ particles is unitary giving back the Cartesian system in the coordinates of $N-1$ particles. Thus the metric tensor remains uniform. The operational implication is that the dependent derivatives $E_{1\alpha}$, $E_{1\alpha 1\beta}$, etc. do not enter into the calculation of dE, d^2E, etc. even though they may have nonzero values calculated in terms of the $3N$ Cartesian coordinate system.

To find the derivatives relative to the remaining external coordinates $\partial E/\partial P_{2x}$, $\partial E/\partial P_{2z}$, $\partial E/\partial P_{3x}$, one rotates the coordinate system (with origin on particle 1) such that particle 2 rotates onto the new y axis (two angles) and particle 3 onto the new yz plane (one angle). Here we show one representative example. The rotation around the x axis which brings the z coordinate of particle 2 to zero can be represented as

$$\begin{pmatrix} \hat{P}_{2y} \\ \hat{P}_{2z} = 0 \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} P_{2y} \\ P_{2z} \end{pmatrix}, \tag{31}$$

where θ is the angle of rotation. Similar to Eq. (30) the chain rule yields $\partial E/\partial \hat{P}_{2z} = 0$ and $\partial E/\partial \hat{P}_{2y} = \partial E/\partial P_{2y}$. In summary, the six external variables have vanishing derivatives in the transformed coordinates, i.e., energy does not directly depend upon their absolute positions, and the equations of motion ought to preserve the initial values of these coordinates.

V. APPLICATIONS

We now examine the application of translational and rotational invariance to algorithms which search for stationary points (minima, maxima, and saddle points) on surfaces. We assume that the surfaces $E(\mathbf{P}_1, \mathbf{P}_2, \ldots \mathbf{P}_N)$ are translation-

ally and rotationally invariant. Particular surfaces of interest to chemists are surfaces of the total electronic energy within the BO approximation in which the effects of electronic motion has been integrated over for fixed values of the nuclear coordinates. Stationary points correspond to the ground and excited electronic states on such surfaces as well provide information about reaction dynamics.

Such surfaces are calculated at every point explicitly in terms of the coordinates of N centers, $\mathbf{P}_K$, usually in terms of $3N$ Cartesian coordinates. The derivatives of the energy are also usually given relative to these $3N$ Cartesian coordinates. Using this information about the energy and its derivatives, the surface stepping algorithms provide a recipe for taking a step along each degree of freedom. A sequence of these steps then leads to the desired stationary point on the surface. Obviously, such a stepping procedure generates unnecessary components of overall translation and rotation of the N particles. Our aim is to find modifications of such a stepping algorithms which take steps that are free from the components of overall translation and rotation. The implication of the results of the previous section is to describe the initial geometry of N particles in a coordinate system of $(3N-6)$ Cartesian internal coordinates $\mathbf{P}=\{P_{2y},P_{3y},P_{3z},P_{K\alpha}\ (K=4,N;\ \alpha=x,y,z)\}^+$ and six external coordinates $\mathbf{Q}=\{P_{1x},P_{1y},P_{1z},P_{2x},P_{2z},P_{3x}\}^+$ with values of zero (i.e., particle 1 on the origin, 2 on the y axis, 3 on the yz plane). We wish to find modifications for the stepping algorithm which constrain the changes in the external variable to zero. We shall use the method of Lagrange multipliers.

Most stepping algorithms[11,12] model the real surface by a finite Taylor expansion in the neighborhood of the current point and then require that each step be a stationary point (of some order) on the model surface. If $\boldsymbol{\lambda}$ is a vector of length six containing six Lagrange multipliers, we require stationary points in $(3N+6)$ variables

$$\begin{aligned}\hat{E}(\mathbf{P},\mathbf{Q},\boldsymbol{\lambda}) = E_0 &+ (\mathbf{g}_P^+\ \mathbf{g}_Q^+)\begin{pmatrix} d\mathbf{P} \\ d\mathbf{Q}\end{pmatrix} \\ &+ \frac{1}{2}(d\mathbf{P}^+, d\mathbf{Q}^+)\begin{pmatrix}\mathsf{H}_{PP} & \mathsf{H}_{PQ} \\ \mathsf{H}_{QP} & \mathsf{H}_{QQ}\end{pmatrix}\begin{pmatrix} d\mathbf{P} \\ d\mathbf{Q}\end{pmatrix} \\ &+ \cdots + (\mathbf{0}^+\boldsymbol{\lambda}^+)\begin{pmatrix} d\mathbf{P} \\ d\mathbf{Q}\end{pmatrix}, \end{aligned} \tag{32}$$

where $\mathbf{0}$ is the zero vector of length $3N-6$ ($3N-5$ for the linear case). Then

$$\nabla\hat{E}_{P,Q} = 0 = \begin{pmatrix}\mathbf{g}_P \\ \mathbf{g}_Q\end{pmatrix} + \begin{pmatrix}\mathsf{H}_{PP} & \mathsf{H}_{PQ} \\ \mathsf{H}_{QP} & \mathsf{H}_{QQ}\end{pmatrix}\begin{pmatrix} d\mathbf{P} \\ d\mathbf{Q}\end{pmatrix} + \cdots + \begin{pmatrix}\mathbf{0} \\ \boldsymbol{\lambda}\end{pmatrix} \tag{33}$$

and

$$\nabla_\lambda \hat{E} = 0 = d\mathbf{Q}. \tag{34}$$

Substituting Eq. (34) in Eq. (33) we arrive at two equations,

$$\mathbf{g}_P + H_{PP}\, d\mathbf{P} + \cdots = 0, \tag{35}$$

$$\mathbf{g}_Q + H_{PQ}\, d\mathbf{P} + \cdots + \boldsymbol{\lambda} = 0. \tag{36}$$

Equation (35) involves *only* the internal variables $\mathbf{P}$ in the $(3N-6)$-dimensional subspace. Furthermore, the form of the equation (which involves no modification for the calculation of the gradient and Hessian elements g_P, H_{PP}) is as if the external variables $\mathbf{Q}$ have been ignored. Therefore, in practice, one starts with initial conformation of the N particles represented completely in terms the $(3N-6)$ internal coordinates $\mathbf{P}$, with zero values for the external coordinates $\mathbf{Q}=0$. The stepping algorithm is performed only in terms of internal coordinates $\mathbf{P}$, which of course leaves the external coordinates unchanged. When a stationary point in this $(3N-6)$ dimension subspace is reached, it is also a stationary point in the $3N$-dimensional space. The values of $\boldsymbol{\lambda}$, should they be needed, can be calculated at a given point for a given step $d\mathbf{P}$. The resulting steps are devoid of any component of overall translation or rotation of any order.

Now we shall apply the above recipe toward locating stationary points on model surfaces. The surface we have chosen is a coupled anharmonic oscillator surface for three particles:

$$\begin{aligned}E(\mathbf{P}_1,\mathbf{P}_2,\mathbf{P}_3) = A_1 r_{12}^2 + A_2 r_{13}^2 + A_3 r_{23}^2 + B_1 r_{12}^4 \\ + B_2 r_{13}^4 + B_3 r_{23}^4. \end{aligned} \tag{37}$$

This surface depends only upon interparticle distances $r_{KJ}=|\mathbf{P}_K-\mathbf{P}_J|$ where $\mathbf{P}_K=(P_{Kx},P_{Ky},P_{Kz})$ refers to the Cartesian coordinates of a particle K, relative to a lab-fixed origin. The surface $E(\mathbf{P}_1,\mathbf{P}_2,\mathbf{P}_3)$ is an explicit function of $3N=9$ coordinates. The function E being translationally

TABLE I. Translation-rotation free path of convergence to the minimum followed by the RFO algorithm on a nine-dimensional model surface of Eq. (37). The internal coordinates are $\mathbf{P}=(P_{2y},P_{3y},P_{3z})$, and starting value $\mathbf{P}_0=(2.0,2.0,2.0)$.

Iteration number	Internal coordinates			Function value
	P_{2y}	P_{3y}	P_{3z}	$E(P_{2y},P_{3y},P_{3z})$
0	2.000	2.000	2.000	35.200
1	1.828	1.803	1.718	24.162
2	1.641	1.604	1.447	16.142
3	1.441	1.403	1.189	10.422
4	1.230	1.198	0.944	6.430
5	1.009	0.990	0.713	3.719
6	0.783	0.776	0.500	1.945
7	0.552	0.554	0.309	0.855
8	0.333	0.328	0.152	0.264
9	0.118	0.121	0.045	0.033
10	0.009	0.010	0.002	0.000
11	0.000	0.000	0.000	0.000

and rotationally invariant, it is possible to choose $3N-6=3$ Cartesian coordinates $\mathbf{P}=(P_{2y}, P_{3y}, P_{3z})$ to be the internal coordinates while the external coordinates $\mathbf{Q}=(P_{1x}, P_{1y}, P_{1z}, P_{2y}, P_{2z}, P_{3x})$ can be taken to be zero. The surface E has a minimum at $r_{12}=r_{13}=r_{23}=0$ which in our internal coordinate system implies that at the minimum $P_{2y}=P_{3y}=P_{3z}=0$.

We have used the RFO algorithm[11] to search for the minimum in the three-dimensional surface of internal coordinates $\mathbf{P}$ with $\mathbf{Q}=0$. Starting from an initial guess $\mathbf{P}_0$, the RFO algorithm requires a solution of an eigenvalue problem

$$\begin{pmatrix} \mathsf{H} & \mathbf{g} \\ \mathbf{g}^{+} & 0 \end{pmatrix} \begin{pmatrix} \Delta\mathbf{P} \\ 1 \end{pmatrix} = \epsilon \begin{pmatrix} \Delta\mathbf{P} \\ 1 \end{pmatrix} \tag{38}$$

for the lowest eigenvalue ϵ for a minimum search. Here, $\mathbf{g}=(\partial E/\partial P_{2y}, \partial E/\partial P_{3y}, \partial E/\partial P_{3z})$ contains the gradients of E relative to the internal coordinates calculated at their current values, while H is the Hessian matrix. The eigenvector gives the change $\Delta\mathbf{P}$ from which a new starting point $\mathbf{P}_0=\mathbf{P}_0+\Delta\mathbf{P}$ is obtained. This process is continued until convergence for which $\Delta\mathbf{P}=\mathbf{g}=0$. In Table I we have shown the path of convergence followed by the RFO algorithm toward the minimum starting from the initial values of the internal coordinates $\mathbf{P}_0=(2.0,2.0,2.0)$. The values for the coefficients of r_{KJ} in Eq. (37) for the surface have been taken to be $A_1=A_2=A_3=1.0$ and $B_1=B_2=B_3=0.2$.

VI. SUMMARY AND CONCLUSION

In this paper we have given relations among derivatives of a property (taken here to be the energy) of an N-body system corresponding to the translational and rotational invariances of the property. As a consequence it is shown that not all derivatives of energy are independent. In particular, for a nonlinear geometry of the N bodies, all unique derivatives of a given order constructed from the set of $(3N-6)$ geometrical variables $\mathbf{P}=(P_{2y}, P_{3y}, P_{3z}, P_{K\alpha};\ K=4, N;\ \alpha=x, y, z)$ are the independent derivatives. All others can be calculated knowing these using the symmetry relations. For example, there are $M(=3N-6)$ independent gradients, $M(M+1)/2$ Hessians, and $M(M+1)(M+2)/6$ independent third derivatives. For linear geometries the $M(=3N-5)$ elements of the set are $\mathbf{P}=(P_{2y}, P_{K\alpha};\ K=3, N;\ \alpha=x, y, z)$.

We have also shown that the elements of $\mathbf{P}$ can also be considered as a bonafide set of internal coordinates in the sense that these coordinates span all possible geometries of an N-body system when the six external coordinates $\mathbf{Q}=(P_{1x}, P_{1y}, P_{1z}, P_{2x}, P_{2z}, P_{3x})$ are taken to be zero. Furthermore, movements along these internal coordinates, which do not alter the values of external coordinates, will include no components of overall translation and rotation of the N bodies. The advantage of these internal coordinates is their Cartesian nature.

We have applied these results toward search for stationary points of a $3N=9$ dimensional surface. Due to the translational and rotational invariance of this surface, a modified surface walker in only three coordinates $\mathbf{P}=(P_{2y}, P_{3y}, P_{3z})$ is sufficient, and walks to a stationary point are translation and rotation free.

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