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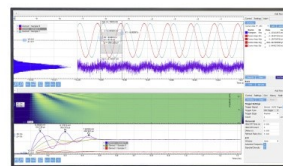
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NOTES

Potential energy surfaces and coordinate dependence

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Properties of a Born–Oppenheimer potential energy surface (PES) such as steepest-descent paths and normal mode frequencies should be independent of the coordinate system employed. If this were not the case then we would obtain different dynamic and thermodynamic properties from different sets of coordinates. However, if the metric tensor of the coordinate system does not correspond to the identity, then extra care is needed to ensure that pathways and frequencies remain coordinate independent. For example, when second derivative matrices (Hessians) are constructed using ordinary partial derivatives of the energy, the eigenvalues can exhibit coordinate dependence. This result does not mean that one particular coordinate system is correct and that others are not. Rather, it means that one should not use ordinary partial derivatives to construct the Hessian when the metric does not correspond to the identity matrix. To obtain relations between physical properties that are independent of the reference frame, *covariant* derivatives should be employed.^{1,2} Although this result is “well known” it seems worthwhile to reiterate it in light of recent papers in this journal where issues of coordinate dependence have been raised.^{3–6}

In the instantaneous normal mode (INM) approach to liquid dynamics^{7–14} ensemble averaged local properties of the potential energy surface (PES) are employed in Taylor series expansions. For example, diffusion constants may be obtained via a short-time fit to an assumed form for the velocity autocorrelation function.^{15–17} An alternative approach has been suggested in which a connection is assumed between the imaginary part of the INM distribution and hopping rates between local minima,¹³ exploiting a model due to Zwanzig.¹⁸

The example of a free diatomic bound by a harmonic potential has been used in previous work to highlight the apparent dependence of normal mode frequencies on the coordinate system.³ If the potential is $V=k(r-r_0)^2/2$ with $r^2=(\mathbf{r}_1-\mathbf{r}_2)^2$ then the Hessian eigenvalues are

$$0, \quad 0, \quad 0, \quad 2k(1-r_0/r), \quad 2k(1-r_0/r), \quad 2k, \quad (1)$$

where unit masses have been assumed for the two atoms. The three zero eigenvalues correspond to overall translation, while the two rotations are coupled to the bond vibration by

a term linear in the gradient, as expected.¹⁹ Only for a stationary point with $r=r_0$ do the two rotational modes exhibit zero eigenvalues.

The problem can be expressed in many other ways, for example in terms of

$$\mathbf{r}_1 \quad \text{and} \quad \mathbf{r}_1 + r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta), \quad (2)$$

or

$$\mathbf{R} \pm r(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)/2, \quad \mathbf{R}=(X,Y,Z), \quad (3)$$

where the corresponding coordinates are the components of \mathbf{r}_1 and r , θ and ϕ in the first case and X , Y , Z , r , θ , and ϕ in the second case. Both of these coordinate systems give the same eigenvalue spectrum as Eq. (1) when the Hessian is calculated from the covariant derivatives

$$H_{ij} = \frac{\partial^2 V}{\partial q^i \partial q^j} - \sum_k \frac{\partial V}{\partial q^k} \Gamma_{ij}^k. \quad (4)$$

Γ_{ij}^k is a Christoffel symbol of the first kind,

$$\Gamma_{ij}^k = \frac{1}{2} \sum_l A^{kl} \left[\frac{\partial A_{jl}}{\partial q^i} + \frac{\partial A_{il}}{\partial q^j} - \frac{\partial A_{ij}}{\partial q^l} \right], \quad (5)$$

A_{ij} are components of the covariant metric tensor, and A^{kl} are components of its inverse. For example, with the coordinates $\{X, Y, Z, r, \theta, \phi\}$ the metric tensor is diagonal with components

$$A_{XX}=A_{YY}=A_{ZZ}=2, \quad A_{rr}=\frac{1}{2}, \\ A_{\theta\theta}=r^2/2, \quad A_{\phi\phi}=\frac{1}{2}r^2\sin^2\theta. \quad (6)$$

The generalized eigenvalue problem that accounts for the nontrivial metric tensor is²

$$\sum_j (H_{ij} - \lambda A_{ij}) c^j = 0, \quad (7)$$

and it is easily verified that solution yields the eigenvalues in Eq. (1) for both the coordinate systems defined in Eqs. (2) and (3).

The use of covariant derivatives and the appropriate metric conserves all the Hessian eigenvalues for proper coordinate transformations, not only those associated with translation and rotation. The covariant first derivative is just the

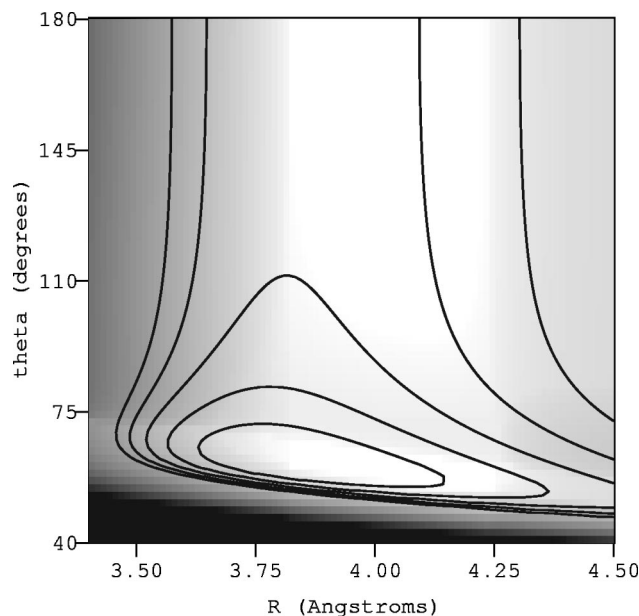


FIG. 1. Equipotential contours and K^1 function for the triatomic cluster bound by the Lennard-Jones potential, replotted from Ref. 27 by Dr. R. J. Hinde. The innermost energy contour is at -0.9 e/atom and the energy increases in successive contours by 0.1 e/atom. The gray scale represents the magnitude of K^1 ; the black areas correspond to $K^1 > 0.25$ and the white areas to $K^1 < 0.001$. The units of K^1 are bits per 10^{-11} s for potential parameters appropriate to Ar. K^1 is proportional to the sum of the moduli of the imaginary normal mode frequencies at every point.

usual partial derivative. Coordinate dependence has been exploited in a number of studies concerning geometry optimization,^{30–33} where the use of simple partial derivatives can produce more efficient convergence. This approach is legitimate, since the stationary points that are located are stationary points in any proper coordinates.

In INM theory the imaginary frequencies are especially important because of their association with barrier crossing events and the calculation of transport properties.^{3–5,20–23} However, this connection is not straightforward, since many of the instantaneous imaginary frequencies may originate from relatively repulsive parts of the potential via anharmonic coupling.^{26–29} In contrast, saddle regions, despite having an imaginary frequency by definition, can be less chaotic or even streaming.^{28,29} This effect is illustrated in Fig. 1. Changing the emphasis from coordinate dependence to finding an appropriate function of the coordinate independent frequencies may be helpful in developing this part of the INM framework.

A further noteworthy feature of the three atom system illustrated in Fig. 1 is that the PES contains a single permutational isomer of the D_{3h} global minimum but three distinct permutational isomers of the linear saddle points. The rearrangements mediated by these saddles connect the global minimum to itself.^{24,25} This peculiarity may affect the “false barriers” described by Gezelter, Rabani, and Berne²¹ for the trimer, but is unlikely to change their results for larger systems.

In another recent paper Ramquet, Dive, and Dehareng have revisited the concepts of bifurcation and branching points on a PES.⁶ They conclude that the location of valley-

ridge inflection points on a steepest descent path depends upon the coordinate system. The coordinate dependence should again disappear if covariant derivatives are used. For example, Ramquet, Dive, and Dehareng consider the two-dimensional potential $-x(y^2+1)$ and the coordinate transformation $u=x+y^2/2$, $v=y$. When the nontrivial metric of the (u,v) coordinate system is accounted for the Hessian eigenvalues are easily shown to be $-x \pm \sqrt{x^2+4y^2}$, independent of the coordinates. Hence there are two zero eigenvalues at the point $(0,0)$. To define curvatures that are preserved under any proper (invertible) coordinate transformation we simply need to take

$$\sum_{ij} D^i H_{ij} D^j / \sum_{ij} A_{ij} D^i D^j, \quad (8)$$

where D^i are the vector components of the direction in question and H_{ij} must be the covariant derivative defined in Eq. (4).

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