COMMENTS

Reduced Mass in the One-Dimensional Treatment of Tunneling

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A recent paper in this journal presented new recommendations for the effective mass for one-dimensional models of tunneling contributions to chemical reactions.[1] Unfortunately the paper involves fundamental misconceptions, and the recommended changes to standard procedures follow from an incorrect derivation rather than from any improvement in modeling the physics. This comment is an attempt to clarify the issues.

It is necessary to distinguish various coordinate systems for describing the nuclear motion of an N-atom system. First consider *atomic Cartesians* $R_{i\gamma}$, with $i = 1, ..., N$, $\gamma = x, y, z$, or R_j, with $j = 1, ..., 3N$. The kinetic energy is

$$T = \frac{1}{2}\sum_{i=1}^{N}\sum_{\gamma} m_i \dot{R}_{i\gamma}^{\ 2} \tag{1}$$

where m_i is the mass of atom i, and an overdot denotes a time derivative. Spectroscopists usually prefer *mass-weighted Cartesians* $q_{i\gamma}$ defined by[2a]

$$q_{i\gamma} = m_i^{1/2} R_{i\gamma} \tag{2}$$

The kinetic energy is

$$T = \frac{1}{2}\sum_{j=1}^{3N} \dot{q}_j^{\ 2} \tag{3}$$

This coordinate system has the disadvantage that "distance" has units of mass$^{1/2}$ length, which is unphysical, but the advantage that it is "isoinertial", i.e., the mass is the same for motion in any direction. A more physical isoinertial coordinate system is the set of *mass-scaled Cartesians* defined by

$$x_{i\gamma} = \left(\frac{m_i}{\mu}\right) R_{i\gamma} \tag{4}$$

for which

$$T = \frac{1}{2}\mu \sum_{j=1}^{3N} \dot{x}_j^{\ 2} \tag{5}$$

Note that the scaling mass μ can take any convenient value. A popular choice is 1 atomic mass unit (amu), and for this choice the numerical value of $x_{i\gamma}$ in angstroms (Å) is the same as the numerical value of $q_{i\gamma}$ in amu$^{1/2}$ Å.

For any of these coordinates, the form of the kinetic energy is unchanged by moving the origin. Thus spectroscopicists often use *mass-weighted Cartesian displacement coordinates* $\Delta q_{i\gamma}$ defined as[2a]

$$\Delta q_{i\gamma} = q_{i\gamma} - q_{i\gamma,\mathrm{e}} \tag{6}$$

where subscript e denotes the classical equilibrium value.

However, if one considers a more general linear transformation, e.g.,

$$\tilde{y}_{i\gamma} = A_i y_{i\gamma} - B_{i\gamma}$$

where y is R, q, or x, then the mass for coordinate $y_{i\gamma}$ must be multiplied by A_i^{-2}. This is the root of the error in ref 1. It does not make sense to discuss the correct choice of "effective mass" unless one specifies the coordinate system. Thus when the authors say that their treatment gives a mass of "$^1/_3$ amu, in contrast to the value of 1 amu obtained by the HVA method",[1] they make precisely this error. In particular, by HVA they denote a standard harmonic vibrational analysis involving normal mode coordinates Q_j with $j = 1, ..., 3N$, which are an orthogonal transformation[2b] of mass-weighted Cartesian displacement coordinates employing a mass unit of 1 amu. The orthogonal transformation is equivalent to

$$Q_k = \sum_{j=1}^{3N} L_{jk}(x_j - x_{j,\mathrm{e}}) \tag{7}$$

where x_j is defined with $\mu = 1$ amu, and where $\mathbf{L}$ is an orthogonal matrix. For this kind of matrix

$$\sum_j L_{jk}^{\ 2} = 1 \tag{8}$$

and therefore the mass does not change, i.e., it remains 1 amu. However, the authors of ref 1 are using a different coordinate system to define the mass, so that, even though they have not introduced any new physics compared to ref 2, they can and do obtain a different mass for motion along the transition vector, which is the imaginary-frequency normal mode. But this is just a trivial difference due to a different scaling of the coordinates, and the authors are wrong to imply that their treatment is more appropriate than the standard one. In fact, the authors obtain different numerical results than the standard treatment for the imaginary frequency and the tunneling correction because they are inconsistent. The inconsistency is most easily explained by a one-dimensional example. The vibrational frequency (in radians/s) is

$$\omega = (F/m)^{1/2} \tag{9}$$

where F is the force constant given by

$$F = \mathrm{d}^2V/\mathrm{d}y^2 \tag{10}$$

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where V is potential energy. We have just explained that the value to use for the mass m depends on the scaling of the coordinate y. When one is consistent, the effect of scaling y is exactly canceled by the change in m in eq 9. The authors of ref 1 take the force constants from a standard harmonic analysis that uses 1 amu, but they take m from their own analysis with a different coordinate system, and thus their ω is wrong.

The coordinates in eqs 1−7 are all special cases of *rectilinear coordinates*, which means that they are *linear* combinations of atomic Cartesians with constant coefficients. The masses corresponding to rectilinear coordinates are constants. Chemists often prefer to use coordinates such as bond distances and bond angles, which are *nonlinear* functions of atomic Cartesians. Such coordinates are called *curvilinear*. (Rectilinear coordinates correspond to straight lines in an atomic Cartesian coordinate system, whereas curvilinear coordinates correspond to curved lines in such a system.) For curvilinear coordinates, the masses depend on geometry, i.e., they are not constants. Furthermore, unlike eqs 1, 3, and 5, there are cross terms in the kinetic energy. Thus the mass array m_i with one index must be replaced by a tensor or matrix with two indices. In fact, the matrix $\mathbf{G}$ is usually defined with units of reciprocal mass such that $(\mathbf{G}^{-1})_{jk}$ tends to $m_j\delta_{jk}$ in the rectilinear case, where δ_{jk} is the kronecker delta.

Harmonic vibrational analysis is suitable for small displacements[2a] from a stationary point, which may be an equilibrium geometry or a saddle point. The standard treatment of harmonic vibrations in curvilinear coordinates[2c] was developed for equilibrium geometries, but it is equally valid at saddle points. In the standard treatment, the geometry dependence of the masses is ignored, and harmonic frequenices are evaluated at the stationary-point geometry. It was appreciated by the original workers that this is sufficient because of the restriction of harmonic analysis to small vibrations,[2c] and in fact the curvilinear and rectilinear treatments always give the same frequencies at geometries where the gradient of V vanishes.[3] In ref 1, the mass is evaluated only at the stationary point as well. As explained above, the source of error is that this mass is used with an inconsistent force constant. If the force constant were evaluated by eq 10 with the same coordinate as used to calculate the mass, then all differences from the standard treatments[2,4,5] would disappear.

All conclusions about tunneling in ref 1 are affected by this fundamental error and are meaningless. However, ref 1 does raise two additional issues that deserve a few comments, namely, the language of "reduced mass" vs "effective mass" and the usefulness (or not) of one-dimensional tunneling treatments.

"Reduced mass" is a term for the appropriate mass corresponding to a linear combination of coordinates involving two or more individual particles (in the present context the particles are atoms). No dynamical approximation is implied. An effective mass is a mass used for some coordinate in order to take account of other degrees of freedom that are not treated explicitly or that are treated approximately (as, for example, in some treatments of tunneling[8]). All masses in ref 1, except the original atomic masses, are reduced masses. The use of the term "effective mass" in ref 1 does not imply a higher-level dynamical treatment but rather an inconsistent treatment of reduced mass.

In general, we can classify tunneling approximations in a number of different ways, but for the present discussion we recognize three levels: (1) one-dimensional approximations, such as the treatments of Wigner[4] and Bell,[5] (2) multidimensional zero-curvature approximations such as the vibrationally adiabatic approximation,[6] and (3) multidimensional corner-cutting approximations such as the small-curvature tunneling (SCT) and large-curvature tunneling (LCT) approximations.[7] Although the derivation of the mass in ref 1 mentions the curvature of the reaction path, the dynamical treatment is identical to the one-dimensional treatment of Wigner[4] but with an incorrect calculation of the imaginary frequency of the saddle point. Reference 1 concluded that one-dimensional tunneling models in the literature have used an inappropriate mass, and the essence of our comment so far is that this conclusion is based on an inconsistent evaluation of the reduced mass. But we want to make it clear that this is not a defense of one-dimensional tunneling models, which are seldom justified in cases where tunneling is significant. The Wigner approximation, which is used exclusively in ref 1, is the simplest of these one-dimensional tunneling approximations, and it is used there for transmission coefficients (κ) as large as 26.99. The Wigner approximation represents the first two terms in a power series

$$\kappa = 1 + c_1\hbar^2 + c_1\hbar^4 + ...$$

approximation to the one-dimensional model, and it is not appropriate to truncate such a series after two terms if the second term is 25.99 times larger than the first (or even if it is twice as large as the first or 0.75 times as large). Furthermore the one-dimensional model is seldom valid even if evaluated correctly because, for reactions with appreciable hydrogenic motion in the reaction coordinate (which are the only cases for which we usually need be concerned about tunneling), the dominant tunneling paths usually sample regions of the potential energy surface where the quadratic expansion about the saddle point breaks down, and this calls for multidimensional[7] treatments. In some cases one can recast such treatments as pseudo-one-dimensional models with effective masses,[9] and such treatments should not be confused with the inconsistent use of reduced mass in ref 1.

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