General Expression for the Effective Mass in the One-Dimensional Treatment of Tunneling Corrections

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A simple and general formalism for the calculation of the "effective mass" necessary for the computation of tunneling corrections by simple one-dimensional models is presented. It is shown that this formalism does not require a priori assumptions regarding the molecularity of the reaction or the relative orientation of the reactive fragments. This method, which we call the Generalized Polyatomic Method, GPM, was used to compute tunneling corrections using the simple Wigner tunneling formalism for the six reactions: $H' + H{-}H \rightarrow H'{-}H + H$, $CH_4 + H \rightarrow CH_3 + H_2$, $CH_4 + OH \rightarrow CH_3 + H_2O$, $CH_3{-}CH_3 + OH \rightarrow CH_3{-}CH_2 + H_2O$ and $HCN \rightarrow CNH$. The results obtained in this work indicate that using the "reduced mass" from a direct vibrational analysis of the transition state instead of the "effective mass" could lead to serious errors in the computation of tunneling corrections. This result is very critical given the popularity of this procedure among researchers computing tunneling corrections in gas-phase reactions. Finally, it is also shown that the simple collinear tri-atomic approach (CTM) developed by Johnston is a special case of our more general GPM method. Given its simplicity and computational efficiency, we recommend GPM as the method of choice when computing "effective masses" to be used in one-dimensional tunneling corrections.

1. Introduction

Since the realization by Hund 63 years ago[1] that tunneling might be important in the kinetics of chemical reactions, the chemical literature has been flooded with fundamental work focusing on theoretical predictions as well as experimental confirmation of the role tunneling plays in chemistry.[2] In particular, semiclassical formalisms such as "Transition State Theory" (TST)[3] corrected by tunneling effects have been applied successfully in the theoretical treatment of the kinetics of reactions involving polyatomic systems.[4]

One of the major assumptions of TST is that in the vicinity of the transition state, motion along a one-dimensional minimum potential energy path (MEP) can be treated as a classical translational motion. This motion can be separated to a good approximation under certain conditions from the rest of the degrees of freedom defining the reactive systems. Along the MEP, the potential energy is a function of a reaction coordinate s which may be though of as a measure of the progress of the reaction. Usually, s is defined so that it is equal to $-\infty$ at the reactants side, zero at the transition state and $+\infty$ at the products side. In certain cases, the potential energy will exhibit a "concave down" shape that will lead to significant tunneling. Tunneling is the result of quantum effects that tend to couple the reaction path coordinate to the remaining degrees of freedom of the reacting system due to curvature along the reaction path. In these cases, the separation of the reaction coordinate from the other degrees of freedom is no longer valid, and tunneling can occur through a variety of paths involving all coordinates. To overcome the limitations of the classical treatment, the separability of the reaction path is assumed and the TST rate constant at a particular temperature T is corrected by a transmission coefficient $\kappa(T)$. Accordingly, the general form of the corrected TST rate constant is

$$k^{\mathrm{SCTST}}(T) = \kappa(T)\cdot k^{\mathrm{TST}}(T) \tag{1}$$

where $k^{\mathrm{SCTST}}(T)$ is the semiclassical transition state theory rate constant, and $k^{\mathrm{TST}}(T)$ is the rate constant computed by the transition state theory formalism in either its conventional[3] or variational form.[5] Classically, reactants going through a MEP and with a reaction coordinate value of s will cross the barrier and reach products only if they have an energy E greater than the potential energy $V_0(s)$. In quantum mechanics there is a finite probability that reactants with $E < V_0(s)$ will tunnel through the barrier and become products. In general, the transmission coefficient $\kappa(T)$ can be written as the ratio between the thermal averages of the quantum and classical transmission probabilities

$$\kappa(T) = \frac{\int_0^\infty P_{\mathrm{Q}}(E)\cdot \exp^{-\beta E}\cdot \mathrm{d}E}{\int_0^\infty P_{\mathrm{C}}(E)\cdot \exp^{-\beta E}\cdot \mathrm{d}E} \tag{2}$$

where $P_{\mathrm{C}}(E)$ and $P_{\mathrm{Q}}(E)$ are the classical and quantum mechanical transmission probabilities respectively, $\beta = 1/k_{\mathrm{B}}T$, and k_{B} is Boltzman's constant. In eq 2, $P_{\mathrm{C}}(E)$ is zero whenever $E \leq V_0$ and unity otherwise. An approximate expression for $P_{\mathrm{Q}}(E)$ can be obtained making use of the WKB semiclassical ap-

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proximation.[6] Inserting the appropriate expressions for the transmission probabilities into eq 2, the following relation for $\kappa(T)$ is obtained[7]

$$\kappa(T) = \beta\cdot e^{\beta V_0(s)}\cdot\int_0^\infty e^{-\beta\cdot E}\cdot P_Q(E)\,dE = \beta\cdot e^{\beta\cdot V_0(s)}\cdot\int_0^\infty e^{-\beta\cdot E}\cdot e^{-2\Theta(E)}dE \quad (3)$$

where: $\Theta(E) = 1/\hbar\int_{s_<}^{s_>}[2\cdot\mu_{\text{eff}}(s)\cdot(V_0(s) - E)]^{1/2}$, $s_<$ and $s_>$ are the classical turning points and $\mu_{\text{eff}}(s)$ is the "effective reduced mass" which is determined by the curvature of the minimum energy path (see below). Analytical solutions for eq 3 are very difficult to derive even when simple potential functions are used in the evaluation of $\Theta(E)$. Significant advances leading to the development of highly accurate models for the computation of the quantum mechanical probability P_Q (and consequently $\kappa(T)$) have been made in the past.[6e,7,8]

Closed form expressions for $\kappa(T)$ have been found in some cases where the shape of the potential has been approximated to certain forms. Thus, Bell[9] has found a very simple formula for $\kappa(T)$ assuming a one-dimensional potential barrier with the shape of an inverted parabola. A similar expression was obtained by Wigner in 1932 using a method which is, to a first approximation, applicable to any form of potential curve.[10] Eckart, was able to provide closed forms for $P_Q(T)$ assuming symmetrical and unsymmetrical variants of an analytical potential energy function.[11] The expressions obtained for $P_Q(T)$ can then be used to compute the transmission factor $\kappa(T)$ by solving the integral in eq 3 numerically. Given their simplicity and relatively small computational cost, these crude models are widely used by researchers throughout the world. This is particularly true in the case of Eckart's formalism, which in some instances has allowed scientists to predict rate constants in reasonable agreement with experimental results.

Tunneling models such as Eckart's, Bell's, or Wigner's require knowledge of the potential energy barrier height, as well as the absolute value of the imaginary frequency $\nu^\ddagger$ corresponding to the transition vector at the transition state. To obtain $\nu^\ddagger$, it is customary to perform a quantum chemical calculation of the harmonic vibrational frequencies using the fully optimized geometry corresponding to the transition state. The direct use of this frequency leads most of the time to incorrect tunneling corrections, given that the vibrational analysis performed by the quantum chemical calculation implicitly uses a "reduced mass" μ_{red}, that does not correspond to the "effective mass" $\mu_{\text{eff}}(s)$, necessary in the calculation of tunneling corrections. Following the harmonic approximation, the expression for $\nu^\ddagger$ can be written as

$$\nu^\ddagger = \frac{1}{2\pi}\sqrt{\frac{F^\ddagger}{\mu_{\text{eff}}(s)}} \quad (4)$$

where $F^\ddagger$ is the force constant corresponding to motion along the transition vector. It is $F^\ddagger$ and not the imaginary frequency that should be extracted from the quantum chemistry calculation. This quantity, together with the correct value for $\mu_{\text{eff}}(s)$ are inserted into eq 4 and the resulting value of $\nu^\ddagger$ is then used with the method of preference in order to obtain the necessary tunneling corrections.

In this work, we discuss a general approximate formalism that leads to simple analytical expressions for $\mu_{\text{eff}}(s)$ which can be used with simple one-dimensional tunneling models such as the ones developed by Bell, Wigner, and Eckart. It is shown that at the lowest level of approximation, $\mu_{\text{eff}}(s)$ depends only on the masses and geometric parameters of the reactive system as well as the tangent to the minimum reaction path. The next level of approximation requires information related to the curvature vector along the reaction path.

Section 2, describes the formalism for computing $\mu_{\text{eff}}(s)$. An example dealing with the simple collinear reaction between an atom and a diatomic is presented in Section 3. In Section 4, the method is applied to 6 different polyatomic cases used as prototypes for a polyatomic reactive system. Imaginary frequencies as well as tunneling corrections at 200 and 300 K computed with Wigner's crude model are also presented and the results are compared with other approximations. Finally, Section 5 summarizes the conclusions of this work.

The main goal of this work is to develop a rigorous and consistent way of computing the "effective mass" to be used in one-dimensional tunneling methodologies. However, there is no attempt to recommend the use of crude one-dimensional tunneling methodologies over their accurate multidimensional counterparts. As explained later, whenever possible, tunneling corrections must be calculated using multidimensional formalisms. Unfortunately, these calculations can become prohibitively expensive in systems with a sizable number of electrons, where information such as energetics and vibrational frequencies should be extracted from the reaction path typically computed with highly correlated ab initio levels of theory. In these cases, scientists have no alternative but to rely on simplified methods that involve the calculation of tunneling corrections based on one-dimensional formalisms. It is within this framework that the method to compute the "effective mass" presented in this work becomes highly useful.

2. Computation of the Effective Mass in the Treatment of One-Dimensional Tunneling

Let's consider a system of N atoms with mass m_α and Cartesian coordinates $x_{\alpha i}$ (with $\alpha = 1, ..., N$; and $i = x, y, z$). The kinetic energy of the system is then given by the following relation[12]

$$T = \frac{1}{2}\Delta\vec{\dot{X}}^{t}\cdot\tilde{M}\cdot\Delta\vec{\dot{X}} \quad (5)$$

where $\Delta\vec{X} = \{\Delta x_{\alpha i}\}$ is the displacement vector and $\Delta\vec{\dot{X}} = \{\Delta\dot{x}_{\alpha i}\}$ the corresponding velocity vector in Cartesian coordinates space. In eq 5, $\Delta\dot{x}_{\alpha i} = \partial\Delta x_{\alpha i}/\partial t$ are the components of the velocity along the Cartesian coordinates, $\tilde{M}$ is a 3N × 3N diagonal matrix with the atomic masses along the diagonal, and the superscript "t" indicates a transpose.

A displacement along a set of 3N-6 internal coordinates $\vec{Q} = \{q_1, q_2, q_3, ..., q_{3N-6}\}$ can be related to the corresponding displacement along the Cartesian coordinates using the following equation

$$\Delta\vec{Q} = \tilde{B}\cdot\Delta\vec{X} \quad (6)$$

where $\tilde{B}$ is Wilson's B-matrix[12] with dimensions 3N-6 × 3N. Because $\tilde{B}$ is a rectangular matrix, it does not have a direct inverse. Usually, the inverse transformation of eq 6 is obtained using the Morse-Penrose inverse transposed B-matrix[13]

$$(\tilde{B}^{t})^{-1} = \tilde{G}^{-1}\cdot\tilde{B}\cdot\tilde{M}^{-1} \quad (7)$$

where the superscript "-1" indicates a matrix inverse and $\tilde{G}$ is Wilson's G-matrix[12] with dimensions 3N-6 × 3N-6

$$\tilde{G} = \tilde{B}\cdot\tilde{M}^{-1}\cdot\tilde{B}^{t} \quad (8)$$

Insertion of eq 7 into eq 6 gives

$$\Delta\vec{X} = (\tilde{B}^{\mathrm{t}})^{-1}\cdot\Delta\vec{Q} = (\tilde{G}^{-1}\cdot\tilde{B}\cdot\tilde{M}^{-1})\cdot\Delta\vec{Q} \qquad (9)$$

Using eqs 5−9, the kinetic energy in internal coordinates can be written as

$$T = \frac{1}{2}\Delta\dot{\vec{Q}}^{\mathrm{t}}\cdot\tilde{G}^{-1}\cdot\Delta\dot{\vec{Q}} \qquad (10)$$

where $\Delta\dot{\vec{Q}} = \partial\Delta\vec{Q}/\partial t$ is the velocity vector in internal coordinates. For a reactive system moving along the MEP, and with a reaction coordinate, s, this vector can be obtained from the following expression

$$\Delta\dot{\vec{Q}} = \frac{\partial\Delta\vec{Q}}{\partial t} = \frac{\partial\Delta\vec{Q}}{\partial s}\cdot\frac{\partial s}{\partial t} = \frac{\partial\Delta\vec{Q}}{\partial s}\cdot\dot{s} \qquad (11)$$

In addition, for any point s_0 on the reaction path, the following Taylor expansion can be used to find the displacement vector $\Delta\vec{Q}(s)$ in internal coordinates corresponding to a new point s

$$\Delta\vec{Q}(s) = \vec{Q}(s) - \vec{Q}(s_0) = \vec{\nu}^{(0)}(s_0)\cdot(s - s_0) + \frac{1}{2}\vec{\nu}^{(1)}(s_0)\cdot(s - s_0)^2 + \cdots \qquad (12)$$

where $\vec{Q}(s_0)$ is the internal coordinate vector corresponding to s_0, $\vec{\nu}^{(0)}(s) = \partial\vec{Q}(s)/\partial s = -\vec{g}(s)/|\vec{g}(s)|$ is the tangent vector that describes the direction of the displacement along the reaction path, $\vec{\nu}^{(1)}(s) = \partial^2\vec{Q}(s)/\partial s^2 = \partial\vec{\nu}^{(0)}(s)/\partial s$ is the curvature vector that describes the direction and magnitude of the bending of the reaction path away from a straight line, $\vec{g}\,(s)$ is the gradient vector (equal to $\partial V(\vec{Q}(s))/\partial\vec{Q}(s)$) and $|\vec{g}(s)|$ is the norm of the gradient. In eq 12, the gradient, tangent, and curvature vectors are computed at $\vec{Q}(s_0)$.

Taking the derivative of eq 12 with respect to the reaction coordinate s, and introducing the result into eq 11 it follows

$$\Delta\dot{\vec{Q}}(s) = [\vec{\nu}^{(0)}(s_0) + \vec{\nu}^{(1)}(s_0)\cdot(s - s_0) + \cdots]\cdot\dot{s} \qquad (13)$$

Substitution of eq 13 into eq 10 gives the following relation for the kinetic energy in terms of the velocity of the reaction coordinate $\dot{s}$

$$T = \frac{1}{2}[(\vec{\nu}^{(0)}(s_0) + \vec{\nu}^{(1)}(s_0)\cdot(s - s_0) + \cdots)^{\mathrm{t}}\cdot\tilde{G}^{-1}\cdot(\vec{\nu}^{(0)}(s_0) + \vec{\nu}^{(1)}(s_0)\cdot(s - s_0) + \cdots)]\cdots\dot{s}^2 \qquad (14)$$

The term in square brackets in eq 14 can be interpreted as the “effective mass” $\mu_{\mathrm{eff}}(s)$ associated with a virtual particle moving along the reaction coordinate with velocity $\dot{s}$

$$\mu_{\mathrm{eff}}(s) = [(\vec{\nu}^{(0)}(s_0) + \vec{\nu}^{(1)}(s_0)\cdot(s - s_0) + \cdots)^{t}\cdot\tilde{G}^{-1}\cdot(\vec{\nu}^{(0)}(s_0) + \vec{\nu}^{(1)}(s_0)\cdot(s - s_0) + \cdots)] \qquad (15)$$

As explained by Bell[14] among others, it is the “effective mass” and not the “reduced mass” which must be used in the treatment of tunneling corrections. As can be observed from eq 15, the magnitude of $\mu_{\mathrm{eff}}(s)$ changes through the MEP and it depends (to second order in the expansion) on the degree of coupling between the tangent and curvature vectors along the reaction path.

Behavior at the Transition State. The immediate result of the formalism discussed above is that even in the case of the simplest one-dimensional tunneling treatment, knowledge of the reaction path is needed since $\mu_{\mathrm{eff}}(s)$ must be computed throughout the path. However, given the significant computational expense that this approach might incur, especially in the case of large polyatomic systems, a further approximation can be made, in which tunneling is assumed to occur only in the vecinity of the transition state (through the top of the potential barrier) and that the “effective mass” is considered to be constant along this region and equal to its value at the transition state. In these cases, only information regarding relative energies and vibrational frequencies of reactants, transition states, and products is necessary. Under these assumptions, a more compact expression for $\mu_{\mathrm{eff}}(s)$ can be obtained. Thus, in the limit of infinitesimally small displacements along the path ($s \rightarrow 0$) and in the vicinity of the transition state ($s_0 \rightarrow 0$), eq 15 becomes

$$\mu_{\mathrm{eff}} = \vec{\nu}^{(0)\mathrm{t}}(0)\cdot\tilde{G}^{-1}\cdot\vec{\nu}^{(0)}(0) \qquad (16)$$

At the transition state, the gradient is zero, and the tangent vector $\vec{\nu}^{(0)}$ must be chosen to be the eigenvector of the Hessian with negative eigenvalue (transition vector).[15] Notice that casting expressions 15 and 16 in Cartesian coordinates leads to

$$\mu_{\mathrm{eff}}(s) = [(\vec{\nu}_x^{\,(0)}(s_0^x) + \vec{\nu}_x^{\,(1)}(s_0^x)\cdot(s_x - s_0^x) + \cdots)^{\mathrm{t}}\cdot\tilde{M}\cdot(\vec{\nu}_x^{\,(0)}(s_0^x) + \vec{\nu}_x^{\,(1)}(s_0^x)\cdot(s_x - s_0^x) + \cdots)] \qquad (17)$$

and

$$\mu_{\mathrm{eff}}(s) = [(\vec{\nu}_x^{\,(0)}(s_0^x))^{\mathrm{t}}\cdot\tilde{M}\cdot(\vec{\nu}_x^{\,(0)}(s_0^x))] \qquad (18)$$

respectively, where $\vec{\nu}_x^{(0)}$, $\vec{\nu}_x^{(1)}$, and s_x are the tangent vector, curvature vector and reaction coordinate in Cartesians. As with expression 16, the tangent vector in eq 18 becomes the eigenvector corresponding to the negative eigenvalue of the Hessian matrix at the transition state.

Expression 16 is similar to the one given by Johnston in his book[2o] where a linear relationship between all velocity components in internal coordinates and the corresponding velocity $\dot{\rho}$ of a “progress variable” has been assumed (as well as a fixed center of mass and angular variables)

$$\mu_{\mathrm{eff}} = \vec{A}^{t}\cdot\tilde{G}^{-1}\cdot\vec{A} \qquad (19)$$

with $\Delta\dot{\vec{Q}} = \vec{A}\cdot\dot{\rho}$, and the vector $\vec{A}$ contains linear proportionality coefficients difficult to determine in the case of polyatomic systems. Johnston has used this approach successfully in the treatment of collinear tri-atomic reactions such as the abstraction

$$\mathrm{H} + \mathrm{H{-}H'} \rightarrow \mathrm{H{-}H} + \mathrm{H'} \qquad (\mathrm{R})$$

where the coefficients $\vec{A}$ can easily be obtained. We call this approach the Collinear Tri-atomic Method (CTM). According to this approach, for a collinear tri-atomic reaction X + YZ → XY + Z, the effective mass μ_{eff} is given by the following relation[2o]

$$\mu_{\mathrm{eff}} = \frac{m_{\mathrm{X}}m_{\mathrm{Z}}(1 + c)^2 + m_{\mathrm{Z}}m_{\mathrm{Y}}c^2 + m_{\mathrm{X}}m_{\mathrm{Y}}}{(m_{\mathrm{X}} + m_{\mathrm{Y}} + m_{\mathrm{Z}})(1 + c^2)} \qquad (20)$$

where m_{X}, m_{Y}, and m_{Z} are the masses of atoms X, Y, and Z respectively, and the parameter c is defined as the ratio of the rate of change of the Y−X bond ($\mathrm{d}R_{\mathrm{XY}}$) to the rate of change of the Y−Z bond ($\mathrm{d}R_{\mathrm{YZ}}$)

$$c = \frac{\mathrm{d}R_{\mathrm{XY}}}{\mathrm{d}R_{\mathrm{YZ}}} \qquad (21)$$

In the case of hydrogen abstraction reactions such as A + H−B → A−H + B, where A and B are polyatomic fragments, Johnston treats the reaction as a collinear tri-atomic system[2n,2o] where the fragments A and B are treated as massive particles X and Z respectively, with a mass equal to the sum of the atomic masses making up the fragments.

The formalism presented in this work provides a general and simple way of computing the linear coefficients (obtained from the tangent vector along the reaction path) without making a priori assumptions about the molecularity of the reactive system, or the relative orientation of the fragments and atoms involved in the reaction. We call this approach the Generalized Polyatomic Method (GPM). The "effective mass" as computed by eq 15 is a function of the reaction coordinate and it is only constant in the vicinity of the transition state (top of the potential energy barrier). Consequently, assuming a constant μ_{eff} when computing tunneling corrections might lead to wrong results, especially in cases where the curvature of the potential energy surface is large, as in heavy-light-heavy abstraction reactions. In these cases, more sophisticated (and computationally intensive) procedures are necessary (see ref 8). Consequently, the use of eq 16 must be exercised with care, keeping in mind that it is just useful within the approximations adopted by one-dimensional tunneling models such as the ones proposed by Wigner, Bell, and Eckart. Furthermore, it is important to remember that the GPM formalism in its simplest form given by eq 16 might not be useful when applied to the calculation of rate constants of reactions characterized by negligible or nonexistent barriers, where the "dynamical bottleneck" has to be computed with the Variational Transition State Theory.

As mentioned before, a common (and in general inappropriate) practice is to use the "reduced mass" associated with the mode corresponding to the imaginary frequency based on a harmonic vibrational analysis of the transition structure. This approach is called the Harmonic Vibrational Analysis (HVA) in this work.

3. The Collinear Tri-Atomic Atom Exchange Case

The reaction between an atom X and a diatomic Y−Z characterized by a collinear transition state and producing X−Y + Z is one of the simplest cases for which analytical expressions for μ_{eff} can be provided.[2o] In this case, there are only two internal coordinates participating in the reaction: R_{XY} and R_{YZ}; the bond lengths between atoms X and Y and atoms Y and Z, respectively. The G-matrix as well as its inverse is given by the following relations

$$\tilde{G} = \begin{bmatrix} g_{11} & g_{12} \\ g_{21} & g_{22} \end{bmatrix}; \tilde{G}^{-1} = \frac{1}{(g_{11}\cdot g_{22} - g_{12}^2)} \begin{bmatrix} g_{22} & -g_{21} \\ -g_{12} & g_{11} \end{bmatrix} \qquad (22)$$

where

$$g_{11} = \frac{1}{m_{\mathrm{X}}} + \frac{1}{m_{\mathrm{Y}}};\ g_{12} = g_{21} = -1;\ \text{and}\ g_{22} = \frac{1}{m_{\mathrm{Y}}} + \frac{1}{m_{\mathrm{Z}}} \qquad (23)$$

Substituting eq 22 into eq 16 leads to

$$\mu_{\mathrm{eff}} = \frac{1}{(g_{11}\cdot g_{22} - g_{12}^2)}\cdot[g_{22}\cdot\nu_1^2 - 2\cdot g_{21}\cdot\nu_1\cdot\nu_2 + g_{11}\cdot\nu_2^2] \qquad (24)$$

where ν_1 and ν_2 are the components of the unit tangent vector, and the expressions for the different elements of $\tilde{G}$ are given by eq 23.

Test Case: H−Atom Abstraction Reaction H + H−H′ → H−H + H′. The H-atom abstraction H + H−H′ → H−H + H′ is the simplest collinear tri-atomic system. This reaction has been extensively studied experimentally throughout the years.[16] In 1935, Pelzer and Wigner[17] developed a theoretical formalism to compute the rate constant of this reaction for a particular temperature. In 1961 Johnston and Rapp[2n] used a variant of a Sato empirical surface developed by Weston[18] together with the CTM method previously described, where the tunneling correction was computed as an average over a series of cuts through the energy surface parallel to the tangent to the minimum energy path at the transition state. In 1968, Shavitt et al.,[2j] performed ab initio molecular orbital calculations to compute the potential energy surface for this reaction as well as isotope effects where tunneling corrections were computed with an Eckart function. Quickert and Le Roy[19] used a scaled version of Shavitt's surface to compute the transmission coefficients numerically, obtaining excellent agreement with experimental isotope effects. Marcus[20] has analyzed the validity of the assumption regarding the vibrational adiabaticity of this reaction. In 1971, Koeppl[21] computed rate constants for this reaction using transition state theory and a very accurate ab initio surface calculated by Liu.[22] The same year, Truhlar and Kuppermann[23] reported the results of their accurate quantum mechanical calculations. More recent work by Garrett, Truhlar and Schatz,[24] reported tunneling corrections and isotope effects for the H_3 system using quantum dynamical calculations in the temperaure range 200 K−300 K. In general, the extensive literature available on this reaction clearly indicates the important role of tunneling, especially at low temperatures.

For reaction (R_1) $m_{\mathrm{X}} = m_{\mathrm{Y}} = m_{\mathrm{Z}} = 1$ amu, and $\nu_1 = -\nu_2$. Thus, eqs 23 and 24 give an μ_{eff} equal to 1/3 amu, in contrast to the value of 1 amu obtained by the HVA method. It is important to note that Johnston's CTM approach also predicts a μ_{eff} equal to 1/3. This is not surprising given that the collinear approach is just a particular case of our more general GPM method.

For this reaction, and the ones involving polyatomic reactants to be described in the next section, full geometry optimizations of reactants and transition states as well as harmonic vibrational frequency calculations were carried out at the MP2/6-311G-(2d,2p) level of theory. In addition, single point energy calculations at the PMP4(SDTQ)/6-311G(3df,2p)//MP2/6-311G-(2d,2p) were used in the calculation of the reaction barrier for the H-atom abstraction reaction H + H−H′ → H−H + H′. This level of theory has been found to provide kinetics parameters in reasonable agreement with experiments for a series of 16 hydrogen abstraction reactions.[4j] All calculations were carried out with the Gaussian 98 suite of programs.[25] Transition state optimized geometries and vibrational frequencies are provided in the Supporting Information section. In the case of the collinear reaction H + H−H′ → H−H + H′, the rate constants, $k(T)$, were computed using the following Canonical Transition State Theory expression[3]

$$k(T) = \kappa(T) \times \frac{k_{\mathrm{B}}T}{h} \times \frac{Q^{\mathrm{TS}}(T)}{Q^{\mathrm{H}}(T)Q^{\mathrm{H}}{}_2(T)} \times \exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right) \qquad (25)$$

where ΔE is the potential energy barrier including zero-point energy corrections and $Q^{\mathrm{X}}(T)$ is the total partition function for species X. In addition, Wigner's tunneling correction $\kappa(T)$, was

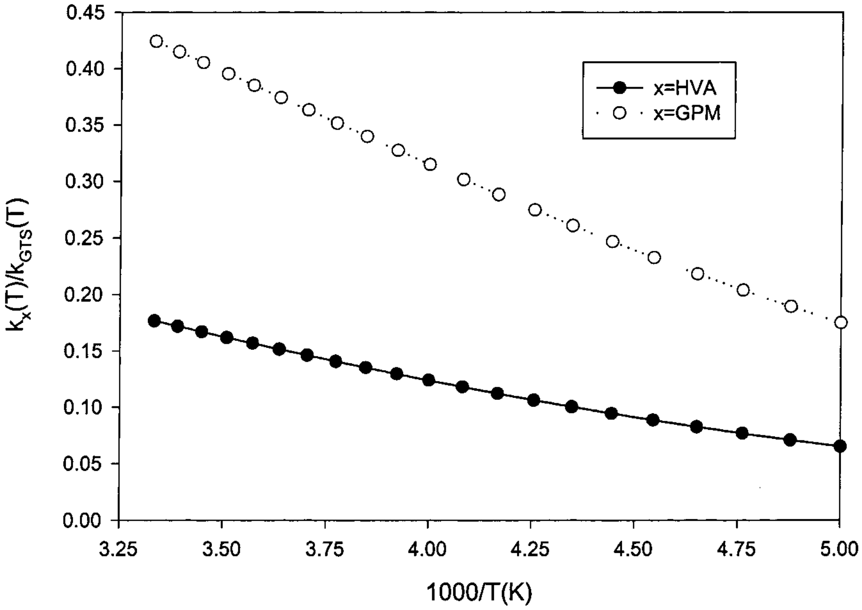

Figure 1. Ratio $k_x(T)/k_{GTS}(T)$ (x = HVA, GPM) as a Function of Temperature for the Reaction $H + H_2 \rightarrow H_2 + H$ in the Temperature Range 200 K−300 K.

computed using the following expression[10]

$$\kappa(T) = 1 + \frac{1}{24}\left(\frac{h\nu^{\ddagger}}{k_B T}\right)^2 \qquad (26)$$

where all the parameters have the same meaning as before.

Figure 1 shows the ratio between the rate constants for the $H + H{-}H'$ reaction computed by our GPM method ($k^{GPM}(T)$) and the accurate rate constants computed by Garrett, Truhlar and Schatz ($k^{GTS}(T)$) using the Centrifugal Sudden (CS) approximation[26] in the temperature range 200 K−300 K. Corresponding ratios between and the HVA rate constants ($k^{HVA}(T)$) and the accurate calculations of Garret, Thrular, and Schatz are also shown in Figure 1. In this temperature range, tunneling processes contribute strongly to the overall rate constant. As can be observed in Figure 1 both, the GPM and the HVA rate constants computed with the simple Wigner tunneling correction are consistently lower than the values reported by the accurate calculations of Garret, Truhlar, and Schatz. This shortcoming in Wigner's and similar formalisms when treating tunneling in reactions exhibiting sizable curvature such as in $H + H_2$ is expected and has been discussed at length in the literature (see for instance ref 23). Given that the purpose of this paper is not to validate a particular tunneling methodology but to demonstrate the need for a better treatment of the effective tunneling mass, we feel that the results obtained with the simple Wigner approach are quite appropriate to achieve this goal. It is interesting to note the overall improvement observed when the effective mass as computed by the GPM method is used in the tunneling treatment. Even at low temperatures, the deviation of $k(T)^{GPM}$ with respect to the accurate rate constant $k(T)^{GTS}$ is significantly smaller than the corresponding deviation for $k(T)^{HVA}$ ($k^{GPM}(T)/k^{GTS}(T) = 0.18$ vs $k^{HVA}(T)/k^{GTS}(T) = 0.07$ at 200 K). These results indicate the importance of the proper treatment of the effective tunneling mass, even for simplified models such as the ones developed by Wigner and Eckart.

4. Reactions Involving Polyatomic Systems

The collinear tri-atomic approach, as originally proposed by Johnston and referred to as CTM1 in this work, assumes a symmetric transition structure A−X−B, where the distance A−B between the heavy fragments changes just slightly in order to keep the center of mass constant, while atom X moves considerably between A and B. Under these constrains, the change in the A−X bond length is equal to the negative of the change in the X−B bond length ($dR_{AX} = -dR_{XB}$). This method then assumes that $\nu_1 = -\nu_2$ as in the case of the reaction $H + H{-}H' \rightarrow H{-}H + H'$ discussed in the previous section. To make this method more general, one could in principle relax this constrain and compute the actual values of the displacements ν_1 and ν_2 from the eigenvector corresponding to the imaginary frequency at the transition state. Given that the collinear tri-atomic approach is still assumed, we refer to this method as CTM2.

To show the importance of computing the appropriate tunneling effective mass, we have computed effective masses, imaginary vibrational frequencies, and Wigner tunneling corrections at 200 and 300 K for the following 5 hydrogen abstraction reactions: $H + H_2$, $CH_4 + H$, $CH_4 + OH$, $CH_2Br_2 + OH$, and $CH_3CH_3 + OH$ using the HVA, CTM1, CTM2, and the GPM approaches described above. In addition, the isomerization reaction $HCN \rightarrow CNH$ is also studied. Table 1 lists the effective masses and the corresponding imaginary frequencies for the 6 reactions computed with the different methods. As previously discussed, the effective mass predicted by the methods CM1, CM2, and GPM in the case of the collinear abstraction $H + H_2$ are exactly the same (1/3 amu.). This is in sharp contrast to the result obtained from the harmonic vibrational approximation calculation, where the effective mass is predicted to be 1 amu. As seen in Table 1, this overestimation in the effective mass leads to an imaginary frequency approximately 1467 cm^{-1} lower than the predicted by the colliner tri-atomic methods (CM1 and CM2) as well as our general polyatomic method (2002 cm^{-1} vs 3469 cm^{-1}).

With the exception of the H-atom abstraction $CH_4 + H$, a significant difference between the masses computed with HVA and the more realistic models CM1, CM2 and GPM is observed. This is particularly true in the case of the H-atom abstraction reaction $CH_2Br_2 + OH \rightarrow CHBr_2 + H_2O$, where the mass predicted by the HVA method is approximately 6 times smaller

TABLE 1: Effective Masses (in amu.) and Imaginary Frequencies (in cm^{-1}) for Six Different Transiton States Computed with the Harmonic Vibrational Analysis Approach (HVA), the Collinear Tri-atomic Methods (CTM1 and CTM2) and the Generalized Polyatomic Method (GPM) Proposed in This Work

transition state	μ_{HVA}	μ_{CTM1}	μ_{CTM2}	μ_{GPM}	$\nu^{\ddagger}_{HVA}$	$\nu^{\ddagger}_{CTM1}$	$\nu^{\ddagger}_{CTM2}$	$\nu^{\ddagger}_{GPM}$
H−H−H	1.00	0.333	0.333	0.333	2002.8	3469.0	3469.0	3469.0
CH_3−H−H	1.133	0.471	1.131	0.820	1703.0	2642.9	1704.5	2002.0
CH_3−H−OH	1.089	0.486	2.050	2.181	1992.9	2986.0	1452.2	1407.8
$CHBr_2$−H−OH	1.079	0.495	3.093	6.857	2199.8	3246.9	1298.9	872.4
CH_3CH_2−H−OH	1.133	0.489	2.013	2.663	1686.8	2566.6	1265.6	1100.3
HCN → CNH	1.172			3.982	1283.0			695.9

TABLE 2: Wigner TunnelIng Corrections for Six Different Reactions Computed at 200 and 300 K with the Harmonic Vibrational Analysis Approach (HVA), the Collinear Tri-atomic Methods (CTM1 and CTM2) and the Generalized Polyatomic Method (GPM) Proposed in This Work

reaction	κ^{200K}_{HVA}	κ^{200K}_{CTM1}	κ^{200K}_{CTM2}	κ^{200K}_{GPM}	κ^{300K}_{HVA}	κ^{300K}_{CTM1}	κ^{300K}_{CTM2}	κ^{300K}_{GPM}
H−H + H	9.66	26.99	26.99	26.99	4.85	12.55	12.55	12.55
CH_3−H + H	7.26	16.09	7.28	9.66	3.78	7.71	3.79	4.85
CH_3−H + OH	9.58	20.26	5.56	5.28	4.81	9.56	3.02	2.90
$CHBr_2$−H + OH	11.45	23.77	4.64	2.64	5.65	11.12	2.62	1.73
CH_3CH_2−H + OH	7.15	15.23	4.46	3.62	3.73	7.32	2.54	2.16
HCN → CNH	4.56	−	−	2.05	2.58	−	−	1.46

than the value predicted by the GPM method (see Table 1). It is interesting to note that the CTM1 method predicts effective masses close to a value of 1/2 amu. for most of the H-atom abstraction reactions with the exception of the symmetric collinear case H + H_2. This is not surprising, given that CTM1 assumes a symmetric transition state characterized by a significant linear displacement of the hydrogen atom between the two heavier (and fixed) fragments. As observed in Table 1, a better agreement with the GPM results is obtained in the case of the CTM2 method, where the collinear approach is still used but the fragments are allowed to move. However, in the case of CH_2Br_2 + OH, it is observed that CTM2 still underestimates the effective mass by a factor of 2 when compared to the GPM result. In addition, the CTM methods cannot be used in reactions such as the HCN → CNH isomerization reaction, where a collinear tri-atomic treatment is not appropriate. Thus, given the simplicity and generality of the GPM method, there does not seem to be of any advantage to use the less realistic CTM formalisms when computing effective tunneling masses. Therefore, we recommend GPM as the method of choice.

Table 2 lists Wigner tunneling corrections computed at 200 and 300 K for the 6 prototype reactions using the 4 different methodologies. As expected, tunneling is more significant at 200 K where it dominates the dynamics of these reactions. Overall, the trends observed are a direct reflection of the trends observed with effective masses. Tunneling corrections computed with the HVA masses deviate considerably from the values obtained with GPM masses. This is particularly true at 200 K where HVA predicts tunneling corrections that are approximately a factor 2−4 off with respect to the GPM values. These results are critical in view of the widespread use of the HVA method among scientists computing tunneling corrections with approximations such as Wigner or Eckart formalisms. Similar trends are observed with the CTM1 results. In the case of the CTM2, a better agreement with the GPM results is obtained, where maximum deviations of a factor of 2 are observed even at 200 K. This is in keeping with the fact that effective masses computed with CTM2 are closer to the values obtained with the more realistic model GPM.

The case of the H-atom abstraction CH_4 + H → CH_3 + H_2 merits some discussion. The results in Table 2 indicate that Wigner tunneling corrections computed with HVA, CTM2 and GPM masses are close in value. This can be traced back to effective masses predicted to be close to 1 amu by the three different methods (see Table 1), indicating that this reaction behaves as a collinear tri-atomic system where the tunneling particle is essentially the hydrogen atom.

5. Conclusions

A general and simple procedure to calculate the "effective mass" necessary in the computation of tunneling corrections using one-dimensional formalisms such as the ones developed by Bell, Wigner, and Eckart has been presented. We call this procedure the general polyatomic method, GPM. This method is sufficiently general and does not assume a priori molecularity or relative orientation of the reactants. It is shown that using the "reduced mass" from a direct vibrational analysis (HVA method in this work) of the transition state instead of the "effective mass" could lead to serious errors in the computation of tunneling corrections. This result is very critical given the popularity of the HVA method among researchers computing tunneling corrections in gas-phase reactions. Finally, it is also shown that the simple collinear tri-atomic approach (CTM) developed by Johnston is a special case of our more general GPM method. Given its simplicity and computational efficiency we recommend GPM as the method of choice when computing "effective masses" to be used in one-dimensional tunneling corrections.

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Supporting Information Available: (i) Table of the harmonic vibrational frequencies computed at the MP2/6-311G-(2d,2p) level of theory for the six transition states considered in this work (Table 1S), (ii) Tables with Cartesian coordinates (in angstroms) corresponding to the fully optimized geometries (at the MP2/6-311G(2d,2p) level) for the six transition states considered in this work (Table 2S−7S). This material is available free of charge via the Internet at http://pubs.acs.org.

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