

Microscopic instanton dynamics in molecules and crystals. Tunneling in NH_3

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A method is proposed for constructing a systematic microscopic description of tunneling processes in molecules and solids. The method is based on the quasiclassical approximation (introduction of instantons) for the nuclear variables and a first-principles calculation of the electronic energy. The inverse splitting of the ground state in NH_3 molecules is calculated. © 1995 American Institute of Physics.

Microscopic (*ab initio*) methods in molecular dynamics (MD) have developed rapidly in the last few years.¹ Repeated attempts have been made to take into account quantum effects by calculating numerically the path integrals in the Feynman representation for the density matrix and the partition function.^{2,3} This computational method is very complicated and “nontransparent” from the physical point of view. In the present paper we propose a systematic and efficient computational method for describing the quantum phenomena associated with tunneling based on the quasiclassical approximation (the concept of instantons⁴). The method does not involve any more complicated computational scheme than the standard molecular dynamics. The quasiclassical approximation in calculations of tunneling processes is standard in quantum chemistry,^{5,6} but the tunneling “path” in this case is postulated. This makes it impossible to study relaxation effects correctly (rearrangement of the adiabatic surface during the tunneling process).

Consider a quantum-mechanical system consisting of nuclei, with masses M_j and coordinates \mathbf{R}_j , and electrons, which is described by the Hamiltonian \hat{H} . Defining the ground-state energy E_0 of the system by the Feynman–Kac formula⁷

$$E_0 = \lim_{\tau_0 \rightarrow +\infty} \left[-\frac{1}{\tau_0} \ln \text{Tr} \exp(-\tau_0 \hat{H}) \right], \quad (1)$$

in which the trace is represented as a path integral, and using the trace over the electronic variables, taking into account the adiabatic approximation (a similar procedure is described in Ref. 8), we find

$$E_0 = \lim_{\tau_0 \rightarrow +\infty} \left[-\frac{1}{\tau_0} \ln \int_{\mathbf{R}(-\tau_0/2) = \mathbf{R}(\tau_0/2)} D\mathbf{R}(\tau) \exp(-S_E[\mathbf{R}(\tau)]) \right], \quad (2)$$

where S_E is the Euclidean action

$$S_E = \int_{-\tau_0/2}^{\tau_0/2} d\tau \left[\sum_j M_j \frac{\dot{\mathbf{R}}_j^2}{2} + i \sum_j \mathbf{A}_j(\{\mathbf{R}_j\}) \dot{\mathbf{R}}_j + U(\{\mathbf{R}_j\}) \right], \quad (3)$$

$$\mathbf{A}_j(\mathbf{R}_j) = i \langle 0 | \frac{\partial}{\partial \mathbf{R}_j} | 0 \rangle$$

is the “vector potential” which is associated with the geometric phase,⁹ $|0\rangle$ is the ground state of the electronic subsystem with fixed nuclear coordinates, and U is the energy (the adiabatic potential) of this ground state which is determined by solving the electronic equation, for example, in the self-consistent field approximation. The term with $\mathbf{A}(\mathbf{R})$ is important only in both cases (degeneracy of the levels) and will be dropped in what follows.

Let the adiabatic potential U have two symmetric minima $\{\mathbf{R}_j^0\} \equiv R_{\pm}$. Reproducing the standard “instanton” derivation from Ref. 4, we then find that the ground state splits into two states that differ in energy by the amount

$$\Delta E = 2K \exp[-W_E], \quad (4)$$

where

$$W_E = \lim_{\tau_0 \rightarrow 0} \int_{-\tau_0/2}^{\tau_0/2} d\tau \sum_j M_j \dot{\mathbf{R}}_j^2 \quad (5)$$

is the truncated Euclidean action (Mauertuis–Euler action) for a trajectory satisfying the equation of motion

$$M_j \frac{d^2 \mathbf{R}_j}{d\tau^2} = \frac{\partial U}{\partial \mathbf{R}_j} \quad (6)$$

with the condition $\{\mathbf{R}_j(\pm \tau_0/2)\} \equiv R_{\pm}$,

$$K = A \omega \sqrt{W_E}, \quad (7)$$

ω is the frequency of small oscillations near the position of equilibrium in the tunneling direction, and A is a numerical factor that depends on the form of the potential [for a potential of the form $U(x) = -Cx^2 + C'x^4$ we have $A = \sqrt{6/\pi}$ (Ref. 4)]. In the one-dimensional case we can derive the following expression by analogy with Ref. 4:

$$K = \lim_{T_0 \rightarrow 0} \sqrt{\frac{\hbar \omega T_0}{2\pi}} \exp[\omega \tau_0(T_0)], \quad (8)$$

where T_0 is the initial kinetic energy at equilibrium. An exact expression for K in the multidimensional case is presented in Ref. 4. From the computational standpoint, because of the unavoidable errors in the determination of W_E , it is pointless to perform a very complicated exact calculation of K from these formulas, and the simple estimate (7), (8) is sufficient. We note that in Refs. 5 and 6 the quasiclassical expression $K = \omega/2\pi$, which is inapplicable for the ground state, was used; for the case of tunneling splitting in NH_3 this leads to an error of more than a factor of 20 as compared with (7).

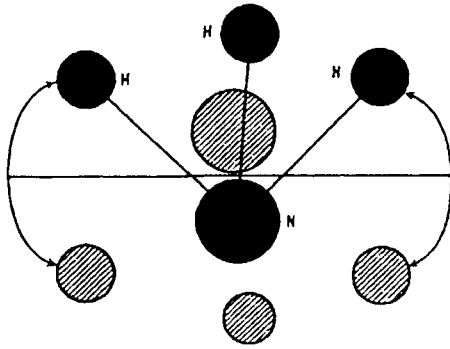


FIG. 1. Schematic diagram of the tunneling path.

If some atoms possess magnetic moments μ_j and the spin degrees of freedom can be assumed to be adiabatic, then they can be included in the analysis by introducing coherent spin states.¹⁰ This leads to the appearance in Eq. (5) of the additional term

$$W_E^{\text{spin}} = i \lim_{\tau_0 \rightarrow \infty} \sum_j \frac{\mu_j}{\gamma} \int_{-\tau_0/2}^{\tau_0/2} d\tau \dot{\varphi}_j (1 - \cos \theta_j), \quad (9)$$

where γ is the gyromagnetic ratio; and φ and θ are the polar angles of the vector μ_j and correspondingly of the additional equations of motion for the spins. We shall examine this question in detail elsewhere.

If the wells are asymmetric and the differences ΔU of their depths are of the order of the tunneling splitting (4), then it can be shown that the resulting splitting in this case is

$$\Delta E = \sqrt{(\Delta U)^2 + 4K^2 \exp(-2W_E)}. \quad (10)$$

As an application of the method, we calculated the tunneling splitting of the ground state of the NH_3 molecule (see Fig. 1). In this case the C_{3v} symmetry is preserved during the tunneling process, and only the initial angle and the initial kinetic energy remain as the initial conditions (the symmetry center of the system is assumed to be at rest). The initial kinetic energy should approach zero. The calculations were performed recently by the well-developed *ab initio* method of molecular dynamics¹¹ using the muffin-tin approximation of the orbitals to describe the basis states. For NH_3 a basis consisting of two sets of *s* and *p* orbitals for each hydrogen atom and three sets of *s* and *p* orbitals and one set of *d* orbitals for the *N* atom was used.

The initial state of NH_3 molecule was matched to a high degree of accuracy, so that the initial forces were $< 10^{-9} \text{ Ry}/a_0$ (a_0 is the Bohr radius). This enabled us to realize the dynamics with a quite low initial kinetic energy. The equilibrium bond lengths and the H-N-H angle were equal to $1.93 a_0$ and 106.0° , respectively. The agreement with experiment ($1.91 a_0$ and 107.0°) is typical for methods of this type. The symmetric normal vibrational modes were calculated by numerically differentiating the total energy with a deviation from equilibrium. The corresponding frequencies were determined to be

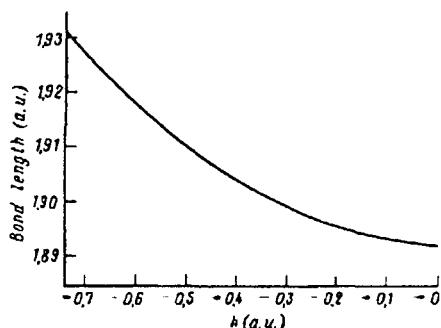


FIG. 2. N-H bond length versus the height h of the pyramid in the tunneling process (in atomic units).

1042 cm^{-1} and 3529 cm^{-1} (the experimental values are 950 cm^{-1} and 3334 cm^{-1}). It was found that, to a high degree of accuracy, the tunneling path can be described as “turning the pyramid inside out” in a manner so that the bond lengths remain approximately constant (Figs. 1 and 2). A calculation for NH_3 gave $W_E = 8.57$, which gives us $\Delta E/\hbar\omega = 1.42 \times 10^{-3}$ using Eq. (8) and $\Delta E/\hbar\omega = 1.53 \times 10^{-3}$ (the experimental value is 0.84×10^{-3}) using Eq. (7) with $A = \sqrt{6/\pi}$. Keeping in mind the uncertainty in the numerical factor in Eq. (7), it is instructive to compare the computed and experimental values of $\ln(\hbar\bar{\omega}/\Delta E)$ (6.55 and 7.09, respectively). On the whole, we can state that in contrast to methods in which the tunneling path was postulated (and the parameters were determined from calculations in the position of equilibrium and in the plane of the transient configuration⁶), the accuracy of the description of the tunneling splitting in the proposed formalism is satisfactory from both the qualitative and quantitative standpoints (the numerical factor is of the order of unity). Note that in our case we have, of course, eliminated the high sensitivity of the computed value of ΔE to the form of the potential along the tunneling path, which was noted in Ref. 6 and which is associated with the nonuniqueness of the latter procedure.

In conclusion, we note that the approach developed here could be helpful in calculating the characteristics of tunneling processes in chemical and biological systems,^{12,13} as well as the quantum diffusion of hydrogen and muons in crystals,¹⁴ quantum effects in ferroelectrics,¹⁵ and in many other problems in molecular and solid-state physics.

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