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Tunneling Splitting in Polyatomic Systems

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Tunneling phenomenon is well recognized as one of the most important quantum mechanical effects from the dawn of quantum mechanics, and it actually plays crucial role in all branches of science from elementary particle physics to biology. In this work, we consider one of the basic phenomena: tunneling splitting in multi-dimensional double well potential and present a canonically invariant instanton theory applicable to vibrationally excited states of polyatomic molecules.

For the ground state tunneling splitting such a theory has been developed recently in [1]. It gives the familiar result $\Delta_0 = \mathrm{B}\exp(-\frac{S_0}{\hbar})$ where S_0 is the classical action along the instanton $\mathbf{q}_0(\tau)$ (periodic classical trajectory in the upsidedown potential). The important achievements of our approach are (i) effective variational iterative procedure to find the instanton $\mathbf{q}_0(\tau)$ and (ii) canonically invariant formula for the pre-exponential factor B which expressed totally in terms of a matrix solution $\mathbf{A}(t)$ of the simple equation

$$\dot{\mathbf{A}}(\tau) = -\mathrm{H}_{\mathbf{qq}} - \mathrm{H}_{\mathbf{qp}}\mathbf{A} - \mathbf{A}\mathrm{H}_{\mathbf{pq}} - \mathbf{A}\mathrm{H}_{\mathbf{pp}}\mathbf{A}\,. \qquad (1)$$

Here $\mathrm{H}_{\mathbf{qq}}, \mathrm{H}_{\mathbf{qp}}, \ldots$ stand for the second derivatives of the classical Hamiltonian function $\mathrm{H}(\mathbf{p},\mathbf{q})$ taken along $\mathbf{q}_0(\tau)$ and, once the instanton trajectory is found, the integration of this equation presents no numerical difficulties. Similar result has been also obtained for the lifetime of unstable complex [2]. It was further shown that due to the iterative procedure (i) *ab initio* potential data can be incorporated into the dynamics calculations without any concomitant extrapolations. Thus, we have formulated a practical *ab initio* semiclassical method which enables us to treat real systems at advanced level of electronic structure theory [3].

In the present work we make the next step and generalize the theory as to be applicable to excited states. In scope of the instanton theory the semiclassical wave function of the vibrationally excited state is shown to be fully determined by a solution of one more (in addition to Eq.(1)) differential equation

$$\dot{U}_k = \left(U^i A_{ij} U^j\right) U_k - [g^{ij} A_{ik} + \partial_k g^{ij} p_{0i}] U_j \qquad (2)$$

where g^{ij} is the metric tensor and p_{0i} is the classical momentum for the instanton trajectory. For N-dimensional system the initial conditions for Eq.(2) can be chosen in N different ways which corresponds

to vibrational excitation of N possible modes. The transformation properties of the solution $\{U_i\}$ are studied and the final canonically invariant formula for the tunneling splitting is derived. Similar to the case of the ground state the present theory can be used in combination with high quality *ab initio* computations to treat polyatomic systems. In comparison with the method for the ground state the only extra job to be done is solution of Eq.(2) which represents no numerical difficulties.

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[2] G.V.Mil'nikov and H.Nakamura, J. Chem. Phys. **117**, 10081 (2002).
[3] G.V. Mil'nikov, K.Yagi, T.Taketsugu, H.Nakamura and K. Hirao. , J. Chem. Phys. **119**, 10 (2003).