

Potential-dependent Activation Energy Calculations by Second Order Gradient Method

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Electron transfer (ET) reactions in solutions or at heterogeneous interfaces and electrodes constitute the core of chemical processes in many applications ranging from electrochemical power generation, such as fuel cells, to biological systems. Knowledge about the electrochemical steps plays a vital role in the analysis of reaction mechanisms and in understanding the involved chemistry. While quantum computations have been extensively used to investigate many non-ET reactions in the reduction steps of oxygen in fuel cells [1-2], corresponding information on ET reactions, despite their significance, seems limited and in a developing stage [3].

The main challenge in dealing with ET reactions is the dependence of rate parameters (activation energies and frequency factors) on the properties of the environment such as the solvent polarizability, the reorganization energy and in particular, the electrode potential. In the first order approximation, the activation energy of an ET reaction ϕ linearly depends on the electrode potential E_e , which leads to the traditional Butler-Volmer equation. However, quantum and semiclassical theories of electron transfer processes indicate a nonlinear dependence of ϕ on the environment parameters [4,5].

In recent years, a new approach has been proposed by Anderson et al. [5] that calculates ϕ as a function of E_e using high level quantum theories, mainly applied to oxygen reduction steps. This model suggests that in an electrochemical reaction such as the oxidation of a surface precursor, the electron transfer occurs when the ionization potential (or electron affinity) of the reactants ψ equals the thermodynamic work function of the electrode, which is a function of its potential. Because the potential energy surface (PES) of the molecule is a function of multidimensional structure coordinates \mathbf{x} , there exists a subset of all configuration points on the PES that satisfy the above electron transfer condition. The transition state of the oxidation reaction \mathbf{x}^* is thus defined as the point in the solution set, where ϕ attains its minimum.

The constrained variation (CV) method, developed by Kostadinov and Anderson [6], introduces a new variable λ to incorporate the electron transfer condition in the Lagrange function Λ defined by

$$\Lambda(\mathbf{x}, \lambda) = \phi(\mathbf{x}) - \lambda[\psi(\mathbf{x}) - eE_e]. \quad (1)$$

The minimization of Λ leads to the solution of the following two equations:

$$\nabla \phi = \lambda \nabla \psi, \quad (2)$$

$$\psi = eE_e. \quad (3)$$

The computational process of this approach is carried out in two steps. In the first step, a point on the PES is found that satisfies the ET condition. Next, a line search algorithm is used to maintain the direction of change in the structure variables perpendicular to the gradient of ψ until it reaches the constrained minimum of ϕ . Although the gradients of ψ and ϕ are calculated by finite differences using a small step size of 0.0004 Å, a shift in potential is observed as the algorithm converges to the corresponding transition states [6]. Since this is a search algorithm in a multidimensional space, a large number of quantum simulations are required to compute the

gradients and find optimum points.

Application and efficiency of the above model for potential-dependent ET reactions can be improved if the transition states are found with a smaller number of trials. Here, we have developed a new algorithm based on the second order expansion of ψ and ϕ around any local point on the PES. The equation for ψ can be written as

$$\psi(\mathbf{x}) = \psi_0 + B_\psi d\mathbf{x} + \frac{1}{2} d\mathbf{x}^T A_\psi d\mathbf{x}, \quad (4)$$

where A_ψ and B_ψ stand for the second and first derivatives of ψ with respect to \mathbf{x} , respectively. The desired change $d\mathbf{x}$ in structure variables is expressed in terms of the undetermined parameter λ using Eq. (2):

$$d\mathbf{x} = (A_\phi - \lambda A_\psi)^{-1} (\lambda B_\psi - B_\phi). \quad (5)$$

Using Eqs. (3) to (5) results in an equation that is a function of λ only. Thus, the proposed algorithm replaces the two-step multi-variable approach of the CV method by a single one-variable step. In addition, it has been observed that this method provides more control on the electrode potential at transition states and converges faster, especially in the case of smooth energy surfaces. The first and second order derivatives of PES are available from the output of the single quantum computations without performing additional calculations necessary in finite difference estimations. Figure 1 demonstrates the potential-dependence of the activation energy for the oxidation/reduction of PtOH₂ precursor hydrogen-bonded to three water molecules using this new method. Five degrees of freedom have been employed in optimizing the structure at the MP2 level of theory in quantum simulations.

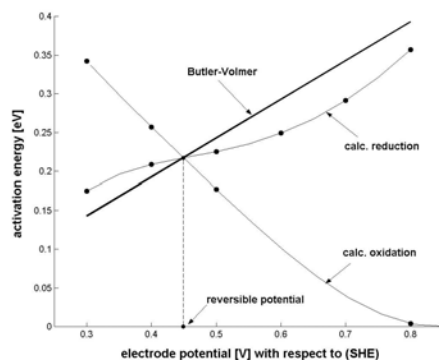


Figure 1. Activation energy at different potentials for oxidation/reduction of PtOH₂·(H₂O)₃. The curves have been fitted to the transition points obtained by the solution algorithm based on the second order expansion of the potential energy surface.

[1] A. Michaelides and P. Hu, *Journal of the American Chemical Society*, 123(18): 4235-4242, 2001.

[2] T. Jacob, R.P. Muller, A. William and W.A. Goddard, *Journal of Physical Chemistry B*, 107(35): 9465-9476, 2003.

[3] Y. Wang and P. Balbuena, *Journal of Physical Chemistry B*, 108(14): 4376-4384, 2004.

[4] D. Dominguez-Ariza, C. Hartnig, C. Sousa, and F. Illas, *Journal of Chemical Physics*, 121(2): 1066-73, 2004.

[5] A.B. Anderson and T.V. Albu, *Electrochemistry Communications*, 1(6): 203-206, 1999.

[6] L.N. Kostadinov and A.B. Anderson, *Electrochemical and Solid-State Letters*, 6(10), E30-3, 2003.