

Quantum chemical studies of Electron Transfer Reactions

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Abstract

The processes of electron transfer reactions are significant in both the fields of chemistry and biology. They play an important part in a variety of systems, including photosynthesis, respiration, and catalysis, among others. Molecular-level comprehension of these reactions is made possible through the application of quantum chemistry studies, which provide a crucial framework. In order to understand the mechanisms, routes, and energetics of electron transfer reactions, this work makes use of modern quantum chemistry methodologies. For the purpose of analyzing the electronic structures of donor-acceptor complexes, the Density Functional Theory (DFT) is applied in conjunction with ab initio approaches. It is necessary to compute important parameters in order to have an understanding of the elements that control the efficiency of electron transfer. These parameters include reorganization energy, activation energy, and electronic coupling. Computational simulations are supported by Marcus theory to offer a thorough description of the kinetics and thermodynamics involved. The data that we obtained illustrate the significant impact that the geometry of molecules, the electrical configuration of molecules, and the impacts of the environment have on the pace and directionality of electron transfer. These discoveries not only contribute to a more fundamental knowledge of electron transfer processes, but they also pave the way for the development of catalytic systems and organic electronic materials that are more effective. Classical, semiclassical, and quantum theories of outer-sphere electron-transfer reactions in polar media are discussed. For each, the Franck-Condon overlap factors for the hexaamminecobalt, hexaammineiron and hexaammine ruthenium self-exchange rates and for the Fe^{2+} - $\text{Ru}(\text{bpy})_3^{3+}$ cross-reaction are evaluated and compared. The quantum effect on the rates is relatively unimportant in the “normal” ΔG° region. Direct sum and saddle-point evaluations of the quantum Franck-Condon factors are made and compared.

KEYWORDS: *quantum chemical, electron, reactions*

Introduction

Kinetics of the heterogeneous electron transfer (ET) is the heart of electrochemistry remaining the most challenging problem from the Tafel time. Mechanisms of interfacial ET are not only of strong interest for theory but also form a framework for understanding the peculiarities of numerous complex multistage electrode processes. Experimental data treated at modern level and comparison with theoretical models can be found in extensive reviews. Since the physical background of the interfacial ET is conceptually quite clear nowadays, the most promising results can be expected when the general theory is applied to certain electrochemical systems. However, even the advanced theory meets with serious difficulties when making quantitative predictions of the electrode reaction rates because of the evident lack of microscopic information about the reaction layer, which leads to uncertainties in the choice of model parameters.

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The answers may be extracted with the help of modern high-level computational chemistry, and first of all by quantum chemical studies of the problems mentioned. Up to now, one can not afford to hope on a 'universal' approach that would predict an exact value of the reaction rate. Nevertheless, the first attempts discussed below demonstrate that the millennium frontier is also a boundary between phenomenological and microscopic (atomic level) description in electrochemical kinetics. We do not feel like to claim to leave behind in XX century traditional phenomenological descriptions like the Frumkin discharge theory. They are still very useful for the treatment of experimental data, and can be adequately combined with microscopic approaches. Our goal is to clarify the physical basis of the phenomenological theories and, in particular to minimize the number of fitting parameters and (or, if possible, to reduce them to zero). We also will discuss the problem of combining some techniques being the routine practice of phenomenological approaches with the Marcus and Levich–Dogonadze–Kuznetsov quantum mechanical theories .

Two works pioneering the application of quantum chemistry in electrochemical science appeared more than two decades ago . In the cluster model of the metal surface was employed for the first time in order to describe the microscopic structure of the EDL compact part. Now the cluster approach is a new powerful tool in theoretical electrochemistry. Several steps towards the molecular cluster modelling of electrified interfaces has been made recently in works]. The authors suggested first a qualitative analysis of the mechanism of electrode process in the framework of group theory. An idea of the quantum chemical calculations of model supermolecules such as 'metal cluster + reactant' has been also put forward in .

Ref should be mentioned among early theoretical attempts to get the quantitative characteristics for certain heterogeneous redox processes by using a simplified description of both reagent and a metal electrode. The authors computed the ET probability for the reduction of a Fe(III)–aquacomplex near a platinum electrode. The electronic structure of the aquacomplex was treated on the basis of the ligand field theory and the free electron model was employed in order to describe the metal wave functions.

This paper is organized as follows. The state-of-the-art in the field of computer modelling of heterogeneous ET is outlined in Section 2. The quantum chemical approaches that are of special interest for electrochemical applications are summarized. Section 3 is devoted mainly to quantum chemical estimations of the innersphere contribution to the total reorganization energy that allow to take account of the effect of asymmetry of the inner-sphere reorganization. In Section 4 the microscopic analysis of the electrostatic terms (the works of approach of reagent and product to an electrode) is reported and some specific features of the Frumkin correction for redox systems with inhomogeneous charge distribution are considered. The problem of the formation of orientational ensembles in the reaction layer is discussed as well. Finally, Section 5 deals with the most complicated problem of the preexponential factor and the analysis of the overlap of reactant orbitals. Special attention is attracted to the problem of the influence of the electrode charge on the transmission coefficient value. In concluding Section 6 specific problems of comparison with experiment are considered. Some details of the approaches under discussion can be found in our recent

original papers. On the other hand, we only mention here another type of some important achievements of quantum chemistry and computer simulations applied to electrochemistry, namely (hydrophilicity of metal electrodes) and (partial charge transfer).

OBJECTIVE

1. to study of quantum chemical
2. to study of electron transfer reactions and effects

LITERATURE REVIEW

Per E M Siegbahn (2016) Proton-coupled electron transfer (PCET) is a general name for a group of rather different reactions occurring in most redox-active enzymes. They all involve electron transfer from a donor to an acceptor, but the degree and character of proton coupling varies strongly from case to case. In the present text, the conventional use of the term PCET will be adopted, in which PCET stresses the fact that connected with an electron transfer (ET) there is a significant proton motion. PCET could be either a concerted one-step process or a twostep process in which there is a first step of ET followed by a second step of proton transfer. A different use of the term PCET exists, where it only stands for the concerted onestep process, but that definition will not be used here. For experimentally observed PCET reactions, the reader is referred to the comprehensive review by Huynh and Meyer.

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Henryk Chojnacki (2015) The search was made for theoretical confirmation of hypothesis that mechanism of cisplatin cytotoxicity is based on dissociative electron transfer (ET) processes. Applying quantum chemical calculations based on supermolecular approach, the reactions mimicking presumed steps of cisplatin activation were evaluated. The electronic structure of model systems: cis- and transplatin with free electrons, hydrated electrons, and water, was studied by using density functional (DFT) within the Huzinaga basis set and GAUSSIAN-09 package. The respective energy was evaluated with the use of B3LYP density hybrid functional. The calculations were performed for gas phase and water solution; the solvent effects were studied by using the polarizable continuum model. Analysis of the energetic and structural parameters of cisplatin vs. transplatin behavior in the model systems leads to conclusion: there are two possible ways of cisplatin biotransformation, hydrolysis and hydrated electron impact, dependent on the medium redox state.

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V. G. Kremenetsky(2018) By the example of quantum-chemical analysis of the model system $\text{MgNbF}_7 + 12\text{MgC}_{12}$, the possibilities of the method of frontier molecular orbitals in studying the mechanism of electron transfer in molten salts are demonstrated. The rich information provided by this method allows recommending it as a tool for testing the hypotheses on the mechanism of charge transfer in electrochemical systems.

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Erika Viviana Godoy Alarcón(2021) It was recently shown that the electron transfer rate constant of an electrochemical reaction and the conductance quantum are correlated with electrochemical capacitance . The association of these two separate concepts has an entirely quantum rate basis that encompasses the electron transfer rate theory as originally proposed by Rudolph A. Marcus. Presently, we demonstrate that this quantum mechanical rate principle can be used to calculate the electron transfer rate constant of a diffusionless heterogeneous electrochemical reaction by taking a specific value of the current–voltage electrochemical curve. The latter is possible because the quantum of conductance is related to the quantum capacitance such that it follows specific electron spin (up and down) and redox state degeneracy rules. Once these rules are settled in the general definition of the quantum rate, the rate of electron transfer is observed to be solely a function of an experimentally measurable quantum capacitance, thus establishing a simple methodology for measuring the electron transfer rate constant. The calculated value of the electron transfer rate is, within the experimental error, in agreement with traditional methods.

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Renat Nazmutdinov(2015) State-of-the-art in the field of quantum chemical modelling of the heterogeneous electron transfer processes is reviewed. Novel approaches originating from interplay between quantum chemistry and modern theory of charge transfer are discussed and illustrated by recent results on the calculation of relevant kinetic parameters for various electrochemical systems. Emphasis is made on the modelling of the inner-sphere reorganization and the works of approach, as well as on the consideration of reaction layer as an orientational ensemble of reagents. Recent approaches to the estimation of electronic transmission coefficient are analyzed. A possibility to employ traditional phenomenological theory to the analysis of experimental data is re-examined in the framework of microscopic treatment.

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Method

For a system having several vibrational normal modes of different frequencies, the direct evaluation of eq 1 can require considerable computing time. However, G can easily be evaluated approximately by replacing the δ function in eq 1 by its Fourier integral representation and then using the saddle-point method. After some manipulations one obtains

$$G = (2\pi Q)^{-1} \int_{-\infty}^{\infty} e^{-i\Delta E t + f(t)} dt \quad (5)$$

and, after using the saddle-point method to approximate the integral, one obtains eq 6,

$$G \approx |2\pi f''(t_0)|^{-1/2} Q^{-1} e^{-i\Delta E t_0 + f(t_0)} \quad (6)$$

where ΔE is the energy (endoergicity) of the transition, t_0 is the stationary phase value of t in the integrand in eq 5, and f, f'' , and t_0 are given in the Appendix. In the case of a self-exchange reaction, product modes in the oxidized species are equivalent to reactant modes in the reduced species so that the formulas simplify considerably. In a thermoneutral self-exchange reaction, $t_0 = -i/2kT$. For other cases eq A6 of the Appendix may be solved numerically, e.g., by iterating from the approximate root

$$t_0 \approx -i(\Delta E + \lambda)/2kT\lambda \quad (7)$$

where $\lambda = \sum_{j=1}^N \lambda_j$ and each $\lambda_j = 1/2 F_j (\Delta Q_j)^2$. Equation 7 gives the exact saddle point in the high-temperature limit, when frequency changes are neglected, and provides a reasonable starting point for iteration in other cases.

Classical Treatment.

When all the degrees of freedom of the system are treated in the classical limit, $h\nu \ll 2kT \rightarrow 0$, and when frequency changes are neglected, eq 5 reduces to eq 8. This

$$G = (4\pi kT\lambda)^{-1/2} \exp[-(\Delta E + \lambda)^2 / 4kT\lambda] \quad (8)$$

equation is similar in form to the classical expression for $G^{2,4}$ but contains energies rather than free energies. This difference arises because eq 5 tacitly assumes zero entropy of reaction, and indeed the initial equation, (eq 1), with its assumption of harmonic oscillators, does not contain any important ΔS° term, whereas the actual ΔS° can be quite large. The classically derived expression is more general in this respect, since it does not assume harmonic oscillations for all motions. As defined earlier, $\lambda_j = 1/2 F_j (\Delta Q_j)^2$ and $\lambda = \sum_{j=1}^N \lambda_j$. It has been shown that frequency changes may be included in an approximate manner by using an average force constant to calculate X_j —rather than using the initial force constant. f_j above is an averaged force constant

$$F_{av} = 2FF' / (F + F') \quad (9)$$

where F and F' are the force constants in the reactant and product states, respectively. The classical value of the Franck—Condon sum (eq 8) is computed by using x 's calculated with average force constants given by eq 9.

“Semiclassical” Treatment

Consider first a one-dimensional case with a coordinate Q . The $\delta(E_m - E_n)$ of eq 1 can be introduced into $|\langle n|m \rangle|^2$. When the commutator of the initial and final Hamiltonians, \mathcal{H}_n and \mathcal{H}_m is neglected, $\delta(E_n - E_m)$ in the integral becomes $\delta(\mathcal{H}_n - \mathcal{H}_m)$, which in turn is $\delta(V_n - V_m)$ since the kinetic energy terms in \mathcal{H}_n and \mathcal{H}_m cancel; V_n and V_m are the potential energies of the reactants and products, respectively. By using the identity $\sum_m |m\rangle \langle m| = 1$, we may reduce the thermally weighted double sum of squared overlap integrals in eq 1 to a single sum over n of $\langle n | \delta(V_n - V_m) | n \rangle$ (eg., see analogous procedure for other problems in ref). These integrals are readily evaluated, yielding a sum of factors proportional to $|\chi_n(Q)|^2$, where Q is that value of the coordinate for which the reactant and product potential energies are equal and χ is the wave function of the reactants. The remaining sum over n in eq 1 is then readily evaluated to yield

$$G = (2\pi\lambda\hbar\omega \coth \gamma)^{-1/2} \exp[-(\Delta E + \lambda)^2 / (2\lambda\hbar\omega \coth \gamma)] \quad (10)$$

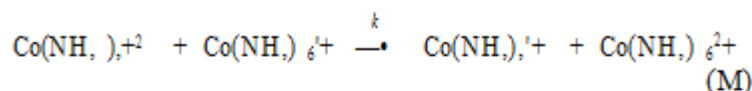
where $y = \hbar\omega/2kT$ and ΔE and λ are defined as in eq 7 but X is for the single mode being considered. Equation 10 is the same as that obtained in ref. by a different procedure. A detailed derivation of eq 10 is given in the appendix.

For systems having two or more frequencies, one obtains a convolution of Gaussians of the form of eq 10. The convolution is itself of the form of eq 10, but $X\hbar\omega\coth y$ must be replaced with $\sum_j \lambda_j \hbar\omega_j \coth y_j$ and X by $\sum_j \lambda_j$. This method of obtaining G 's, which originated in the theory of optical spectra of solids,²⁹ is sometimes termed "semiclassical" because of neglect of commutators of \mathcal{H}_n and \mathcal{H}_m , although the term "semiclassical" has a variety of other meanings (corresponding to other approximations) in the literature.

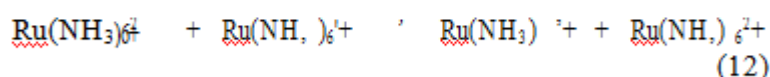
Discussion

We now proceed to consider quantum effects in four particular cases of chemical interest: the hexaamminecobalt and hexa- ammineruthenium self-exchange reactions, the $\text{Fe}^{2+/3+}(\text{aq})$ self- exchange reaction, and the $\text{Fe}^{2+}-\text{Ru}(\text{bpy})_3^{3+}$ cross-reaction.

Hexaamminecobalt Self-Exchange Reaction. The large dif- ference between the rates of self-exchange reactions 11 and 12 has long been a matter of interest in the theory of electron-transfer rates.



$$k = 10^8 \text{ M}^{-1} \text{ s}^{-1} \text{ at } 25^\circ \text{C}$$



$$k_2 = 10^1 \text{ M}^{-1} \text{ s}^{-1} \text{ at } 25^\circ \text{C}$$

In the quantum theory described earlier, the rate constant involves the product of the square of an electronic exchange integral and a sum of Franck—Condon factors. It has been sug- gested that the electronic factor for reaction 11 may be small because of spin multiplicity restrictions." Further, the Franck— Condon term is much smaller for the Co reaction than for the Ru reaction because of the larger change in geometry from $\text{Co}(\text{NH}_3)_6^{2+}$ to $\text{Co}(\text{NH}_3)_6^{3+}$ (cf. Table I).

Buhks et al. evaluated the Franck—Condon sums, G , for re- actions 11 and 12, by using the saddle-point method described earlier. They found $G(\text{Co}) \approx 7 \times 10^{-18}$ cm and $G(\text{Ru}) = 1.5 \times 10^{-10}$ cm so that the ratio of Franck—Condon sums contributes a factor of ca. 10^{-8} to the ratio k_1/k_2 . But they also found that the classical value of $G(\text{Co})/G(\text{Ru})$ was $\sim 10^{-3}$. The gross dis- crepancy between the classical and quantum values, a factor of 1000, led them to suggest that $G(\text{Co})$ is heavily dependent on quantum effects. There is clearly some error in either the classical or the quantum Franck—Condon factors of ref 5 since tunneling

effects should cause G(Co)/G(Ru) to be larger in the quantum case than in the classical one, yet a smaller value was found for the quantum case in ref 5.

Actually, we have found that the large classical value of ref 5 for G(Co)/G(Ru) is the result of using the inaccurate estimate (28.5 kJ/mol) of Styne and Ibers¹ for the hexaamminecobalt internal reorganization energy. The latter seem to have treated the bond length reorganization energy in the hexaamminecobalt ions as containing only diagonal terms $\frac{1}{2} \sum_{i=1}^6 f_r (\Delta q_i)^2$, where Δq_i is the displacement in the *i*th Co—N bond length and f_r is the Co—N bond force constant. But the reaction coordinate is actually the symmetric stretching normal mode, and when expressed in terms of bond modes cross-terms are obtained. The totally symmetric F matrix force constant $F_{A_{1g}}$ is given in terms of generalized valence force field (GVFF) constants by eq 13,³² where f_r is the

$$F_{A_{1g}} = f_r + 4f_{rr'} + f_{rr} \quad (13)$$

diagonal force constant and f_{rr} and $f_{rr'}$ are off-diagonal force constants. $f_{rr'}$ denotes interaction between displacements perpendicular to each other. f_{rr} denotes interaction between displacements on the same line. The symmetric stretching normal-mode force constant F_1 involves both the F and G matrix elements and equals $F_{A_{1g}}/m_L$,³² where m_L is the mass of one ligand. The bond length reorganization energy is $\frac{1}{4} F_1 (\Delta Q_1)^2$, where ΔQ_1 , the normal-mode displacement, is $(6m_L)^{1/2} \Delta q_i$ ³² (all six Δq_i 's are equal). Thus, this reorganization energy equals $\frac{1}{4} (f_r + 4f_{rr'} + f_{rr}) (\Delta q_i)^2$. It thereby involves both diagonal (f_r) and off-diagonal (f_{rr} and $f_{rr'}$) GVFF force constants, and the latter are almost as important as the former. Accordingly, we have made a comparison of the more correct classical value with the quantum sum, as well as with the semiclassical sum for G.

In the high-temperature (classical) limit, the Franck-Condon factors usually depend mainly on modes in which the product potential is displaced in coordinate space relative to the reactant potential (i.e., $X \neq 0$). In the cobalt- and ruthenium-hexaammine self-exchange reactions only the solvent modes and the totally symmetric A_{1g} internal modes have nonzero λ 's. Changes of frequency in the other modes would also make some contribution to G, of course, and as an example we include the modes of E_g and F symmetry later in quantum calculations of G. The approximate classical expression for G (eq 8) cannot treat modes for which $X = 0$.

Using the known A_{1g} stretching frequencies (cf. Table I) for cobalt(II/III) hexaammine, we calculated the A_{1g} symmetry force constants F_{III} and F_{II} (i.e., the $F_{A_{1g}}$ for oxidation states 111 and 11) to be 2.45×10^3 and 1.28×10^3 N/m, respectively. Using the average force constant of eq 9 and the Co-N bond lengths in Table I, we found the internal reorganization energy to be about 48 kJ/mol³⁵ (instead of the 28.5 kJ/mol calculated in ref 1). By analogous calculation, the ruthenium(II/III) hexaammine internal reorganization energy is found to be 2.5 kJ/mol. The total outer-sphere λ 's for the cobalt and ruthenium reactions have recently been estimated as 117 and 113 kJ/mol, respectively. With use of these energy parameters, eq 8

yields as a classical result $G(\text{Co})/G(\text{Ru}) \approx 5 \times 10^{-9}$, which is in reasonable agreement with the quantum result, both as given by Buhks et al. and as calculated below.

In order to assess the accuracy of the saddle-point method for the hexaamminecobalt system, we compared the value of G obtained by direct sum with that obtained by saddle-point integration. For simplified models consisting of only the A_{1g} internal mode or of both the A_{1g} and one of the two degenerate E_g internal modes, both the direct and saddle-point calculations have been performed. (For the E_g modes ΔQ_i is zero, if in the transition state each reactant has octahedral symmetry, but $\Delta \omega_i$ is nonzero.) The results are given in Table II. At least for the models in this table the saddle-point evaluation is a very good approximation.

Conclusion

We have shown that the Franck-Condon contributions to the rates of the hexaamminecobalt, hexaammineruthenium, and hexaquoiron self-exchange reactions at 300 K can be reasonably well approximated by the classical expression (factors of 4.3, 1.2, and 3.5, respectively). These corrections are relatively minor, in view of the uncertainties in the various quantities involved in the rate expression. A nonadiabatic model was assumed, but analogous results would be expected for an adiabatic model. Also for these systems, we have seen by direct comparison with the exactly evaluated quantum sum of Franck-Condon terms that the saddle-point approximation is a very good approximation to the exact sum. The “semiclassical” approximation (eq 10) is a poor one for self-exchange reactions such as Fe^{2+} - Fe^{3+} . The quantum effect on the cross-reaction relation (eq 17) for hexaquoiron(II) with tribipyridylruthenium(III) is negligible (a factor of 0.94), since some cancellation of quantum effects occurs in the calculation of cross-reaction rates. We conclude that a reasonable order of magnitude estimate for the contribution of configurational changes of high-frequency quantum modes in the first coordination layer, for typical metal-ligand frequencies, to the rate constant can be provided by a classical expression. Preexponential factors and activation energies are expected to be more sensitive to use of the classical approximation (they are to other approximations also) and will be discussed in a subsequent paper.

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