

Dynamics of charge transfer: Rate processes formulated with nonequilibrium Green's functions

Sina Yeganeh and Mark A. Ratner^{a)}

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113 and Center for Nanofabrication and Molecular Self Assembly, Northwestern University, Evanston, Illinois 60208-3113

Vladimiro Mujica^{b)}

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113; Center for Nanofabrication and Molecular Self Assembly, Northwestern University, Evanston, Illinois 60208-3113; and Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439-4831; and Universidad Central de Venezuela, Facultad de Ciencias, Escuela de Química, Apartado 47102, Caracas 1020-A, Venezuela

(Received 16 February 2007; accepted 5 April 2007; published online 27 April 2007)

The authors examine the connection between electron transport under bias in a junction and nonadiabatic intramolecular electron transfer (ET). It is shown that under certain assumptions it is possible to define a stationary current that allows the computation of the intramolecular transfer rate using the same formalism that is employed in the description of transport. They show that the nonequilibrium Green's function formalism of quantum transport can be used to calculate the ET rate. The formal connection between electron transport and electron transfer is made, and they work out the simple case of an electronic level coupled to a vibrational mode representing a thermal bath and show that the result is the same as expected from a Fermi golden rule treatment, and in the high-temperature limit yields the Marcus electron transfer theory. The usefulness of this alternative formulation of rates is discussed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2735606]

With the interest in molecular electronics and electron transport in single molecule junctions, there has been much discussion of the similarities between electron transport through molecules and electron transfer (ET) between/in molecules as traditionally understood in a chemical reaction. The similarities have been stressed in theoretical works,¹⁻⁸ and there have been some preliminary discussions of the links between the formalisms commonly used to describe both processes.⁹⁻¹²

Electron transfer reactions in the condensed phase occur as a response of a molecule to environmental polarization fluctuations typically produced in a solvent or a solid matrix. As a result, the electronic density of the molecule fluctuates, and charge transfer can occur. This process is in many ways similar to molecular conductance where electron transport occurs between two electrodes connected by a molecular bridge, and bias voltage causes an imbalance in chemical potential, driving electrons through the molecule.

Indeed, the formalism commonly used in the calculation of current in electron transport, the nonequilibrium Green's function (NEGF) method, has been applied to the problems of x-ray absorption fine structure¹³⁻¹⁵ and calculating the reaction probability for photoinduced surface reactions.¹⁶ Keldysh Green's functions have also been used in calculating transition probability expressions for vibrationally modulated ET.¹⁷ Herein we present a simple model that reproduces the Fermi golden rule (FGR) result for the electron transfer of two electronic states with harmonic potentials, displaced but

with the same frequency,¹⁸ and we discuss the approximations necessary to obtain the Marcus ET theory^{19,20} using NEGF. Thus, a formal connection between transport and rate processes is made. Besides providing a pedagogical link, the NEGF formalism allows the straightforward inclusion of electron-electron interactions in the self-energy framework,²¹ an alternative to the correlated electronic structure methods currently used in calculating electronic couplings in ET.²²⁻²⁸

We begin with the following single-state Hamiltonian:

$$H = \varepsilon_0 c^\dagger c + \omega_0 a^\dagger a + \sum_{k \in L,R} \varepsilon_k c_k^\dagger c_k + M(a + a^\dagger) c^\dagger c + \sum_{k \in L,R} (V_k c_k^\dagger c + \text{H.c.}), \quad (1)$$

where c^\dagger/c are creation/annihilation operators for the single electronic state with energy ε_0 , a^\dagger/a are creation/annihilation operators for the single vibrational mode with frequency ω_0 , and c_k^\dagger/c_k are creation/annihilation operators for electrons with energy ε_k in the left and right reservoirs, which are used to impose steady-state conditions.^{1,10,16,29} M and V_k are couplings of the single electronic state to the vibrational degree of freedom and the reservoirs, respectively.

We proceed by applying a canonical transformation,^{30,31}

$$\bar{H} = e^O H e^{-O}, \quad (2)$$

$$O = \frac{M}{\omega_0} c^\dagger c (a^\dagger - a), \quad (3)$$

resulting in the transformed Hamiltonian (dropping a constant energy term),

^{a)}Electronic mail: ratner@northwestern.edu

^{b)}Electronic mail: vmujica@northwestern.edu

$$\bar{H} = \bar{\varepsilon}_0 c^\dagger c + \sum_{k \in L,R} \varepsilon_k c_k^\dagger c_k + \sum_{k \in L,R} (\bar{V}_k c_k^\dagger c + \text{H.c.}), \quad (4)$$

where the following definitions have been used:

$$\bar{\varepsilon}_0 = \varepsilon_0 - \frac{M^2}{\omega_0} \equiv \varepsilon_0 - \lambda, \quad (5)$$

$$\bar{V}_k = V_k X, \quad (6)$$

$$\bar{c} = cX, \quad (7)$$

$$X = e^{-M/\omega_0(a^\dagger - a)}, \quad (8)$$

where λ is equivalent to the outer-sphere reorganization energy.

As a result of the exponential term in \bar{V}_k , Wick's theorem does not apply and hence no Dyson equation exists for the electronic Green's function.³² Treating this situation properly in the limit of strong electron-phonon and strong electron-lead coupling (or strong electron-electron interaction) is a difficult problem, which can be approached with numerical renormalization group methods.³³ In the ET situation, the leads represent reservoirs of initial and final states, and in nonadiabatic ET with small couplings between states, the effect of renormalization will be small on the electron-reservoir coupling,³⁴ $\bar{V}_k \approx V_k$. [If desired, a Bloch average could be performed over the phonon X operators, resulting in $\bar{V}_k \approx V \exp(-S(N_B + 1/2))$, where $S = (M/\omega_0)^2$ is the Huang-Rhys factor and $N_B = [\exp(\beta\omega_0) - 1]^{-1}$ is the Bose distribution function.] We, however, simply ignore the renormalization of electron-lead coupling,⁸ and by dropping the X operator renormalization of V_k we are able to proceed with our approximate transformed Hamiltonian,

$$\bar{H} = \bar{\varepsilon}_0 c^\dagger c + \sum_{k \in L,R} \varepsilon_k c_k^\dagger c_k + \sum_{k \in L,R} (V_k c_k^\dagger c + \text{H.c.}). \quad (9)$$

The retarded electronic Green's function is given by³¹

$$G^r(t) = -i\theta(t) \langle [c(t), c^\dagger(0)]_+ \rangle_H = -i\theta(t) \langle [\bar{c}(t), \bar{c}^\dagger(0)]_+ \rangle_{\bar{H}}, \quad (10)$$

where $\theta(t)$ is the Heaviside function. The anticommutator yields two terms corresponding to electron transport and hole transport,³⁵ but here we only consider electron transport, where the state is always unfilled,

$$G^r(t) = -i\theta(t) \langle \bar{c}(t) \bar{c}^\dagger(0) \rangle_{\bar{H}} = -i\theta(t) \langle c(t) X(t) c(0) X(0) \rangle_{\bar{H}}. \quad (11)$$

Taking the Born-Oppenheimer approximation, so that averages over electron and nuclear dynamics can be separated, Green's function can be found following standard derivation:³¹

$$G^r(t) = -i\theta(t) \sum_{l=-\infty}^{\infty} e^{-it(\bar{\varepsilon}_0 + l\omega_0) - S(2N_B + 1)} I_l [2S\sqrt{N_B(N_B + 1)}] e^{\beta l \omega_0 / 2}, \quad (12)$$

where I_l is the modified Bessel function.³⁶ At zero temperature, the following simpler expression results

$$G^r(t) = -i\theta(t) \sum_{l=0}^{\infty} e^{-it(\bar{\varepsilon}_0 + l\omega_0)} \frac{e^{-S} S^l}{l!}. \quad (13)$$

Note that we do not include the broadening from lead-molecule coupling typically found in molecular junction treatments, as the ET system is analogous to the quantum dot case where the effect of coupling to the leads (steady-state reservoirs) is small in the molecular region.

Since the canonical transformation has been made and the lead-molecule renormalization has been dropped, we have a noninteracting system³⁷ and the Meir-Wingreen formalism³⁸ converges to the Landauer result^{39,40} for the current,

$$I = \frac{e}{\hbar} \int_{-\infty}^{\infty} \frac{dE}{2\pi} [f_L(E) - f_R(E)] \text{Tr}(G^a \Gamma_R G^r \Gamma_L), \quad (14)$$

$$= -\frac{2e}{\hbar} \int_{-\infty}^{\infty} \frac{dE}{2\pi} [f_L(E) - f_R(E)] \text{Im} \left[\text{Tr} \left(\frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} G^r \right) \right], \quad (15)$$

where the advanced Green's function is given by $G^a = (G^r)^*$ and the Fermi functions of the left and right leads are given by $f_{L,R}(E)$. The couplings to the left and right leads are subsumed into $\Gamma_{L,R}$, given by

$$\Gamma_{L,R} = 2\pi \sum_{k \in L,R} |V_k|^2 \delta(E - \varepsilon_k). \quad (16)$$

We next transform the current equation to yield an equation for the transition probability rate, W . The current and rate are both fluxes, related by $W = I/e$.^{10,11} The steady state rate is calculated by

$$W_{i \rightarrow f} = -\frac{2}{\hbar} \int_{-\infty}^{\infty} \frac{dE}{2\pi} [f_i(E) - f_f(E)] \text{Im} \left[\frac{\Gamma_i \Gamma_f}{\Gamma_i + \Gamma_f} G^r \right], \quad (17)$$

$$= -\frac{2}{\hbar} \int_{-\infty}^{\infty} \frac{dE}{2\pi} \left(\frac{\Gamma_i \Gamma_f}{\Gamma_i + \Gamma_f} \right) \text{Im}[G^r], \quad (18)$$

where subscripts i/f correspond to initial/final states, and we have taken in steady-state that $f_i = 1$ and $f_f = 0$.¹⁰ The left and right electrodes have been replaced by initial and final state reservoirs. Figure 1 illustrates the model system where there is a final state reservoir to force steady-state conditions, analogous to an infinitely dense product density of states in FGR treatments⁴¹ as well as a discrete initial state. In the FGR regime where a rate can be defined, the final state

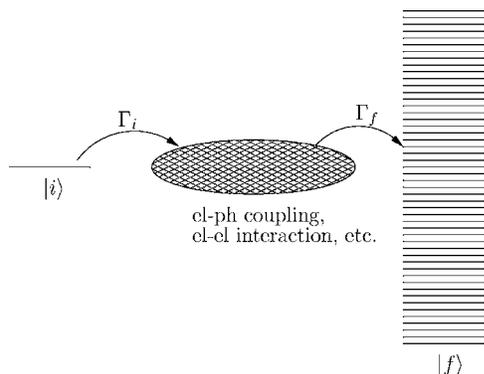


FIG. 1. The model system used in current/rate calculations is shown. The initial/final reservoirs correspond to left/right electrodes; however, note that the initial state is discrete, representing a well-defined reactant state.

coupling will be much stronger than the discrete initial state coupling so that

$$\Gamma_i \Gamma_f / (\Gamma_i + \Gamma_f) \approx \Gamma_i = 2\pi |V_i|^2 \delta(E - E_i). \quad (19)$$

The equation for transition probability rate in steady state can then be written as

$$W_{i \rightarrow f} = -\frac{2}{\hbar} |V_i|^2 \text{Im}[G^r(E_i)]. \quad (20)$$

Note that only one coupling remains in the rate expression—physically, the loss of any dependence on V_f is reasonable since the final state reservoir is merely a tool for imposing a continuum of final states to attain a steady-state rate, and V_i represents the only relevant state coupling, equivalent to the electronic coupling matrix element, H_{if} . Thus, the lead-molecule-lead model of a molecular junction can be reduced to a lead-molecule in the FGR limit of ET.

It is instructive to go through the rate constant formalism in the zero temperature case for simplicity. Equation (13) can be Fourier transformed,

$$G^r(E) = \sum_{l=0}^{\infty} \frac{e^{-S} S^l}{l!} [E - \bar{\varepsilon}_0 - l\omega_0 + i\eta]^{-1}, \quad (21)$$

where $\eta \rightarrow 0^+$ is the positive infinitesimal. Thus, inserting the appropriate zero temperature retarded Green's function, and making the association $|V_i|^2 \equiv |H_{if}|^2$, we find

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} |H_{if}|^2 \sum_{l=0}^{\infty} \left(\frac{e^{-S} S^l}{l!} \right) \delta(E_i - \bar{\varepsilon}_0 - l\omega_0). \quad (22)$$

If we had included the effect of lead broadening on the molecular levels in Eq. (13), the delta function would be replaced by a Lorentzian with width $\Gamma/2$. This result is similar to the Lorentzian broadening expected from relaxation effects.⁴² The energy balance in the delta function can be rewritten by referring to Fig. 2, from which we write

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} |H_{if}|^2 \sum_{l=0}^{\infty} \left(\frac{e^{-S} S^l}{l!} \right) \delta(\Delta - l\omega_0), \quad (23)$$

where Δ is the exoergicity of the reaction. Equation (23) is precisely the result expected from a FGR treatment of the

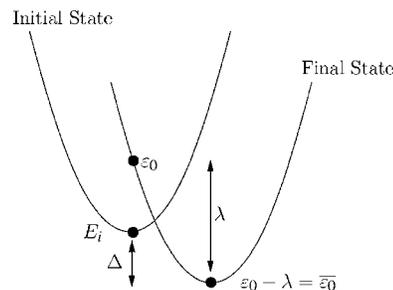


FIG. 2. Marcus parabolas showing the polaron shift to $\bar{\varepsilon}_0$ are shown. The exoergicity Δ can be related to an applied voltage with a specific potential profile, as discussed in the text and in Fig. 3.

displaced harmonic oscillator within the Condon approximation.

One interesting note can be made regarding the relationship between the exoergicity in ET (equivalently, the free energy change for our case of displaced harmonic oscillators) and the voltage in molecular conductance. The exoergicity and voltage, V , can be related by $V = \Delta/e$ for a specific voltage profile: this equivalence holds when the voltage drop is entirely between the initial state (left electrode) and the molecular (device) region, as shown in Fig. 3.

We proceed to the finite temperature case where we use Eq. (20) with the full form of $G^r(E)$,

$$G^r(E) = \sum_{l=-\infty}^{\infty} e^{-S(2N_B+1)} I_l [2S\sqrt{N_B(N_B+1)}] e^{\beta l \omega/2} [E - \bar{\varepsilon}_0 - l\omega_0 + i\eta]^{-1}, \quad (24)$$

and accordingly we find

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} |H_{if}|^2 \times \sum_{l=-\infty}^{\infty} e^{-S(2N_B+1)} I_l [2S\sqrt{N_B(N_B+1)}] e^{\beta l \omega/2} \delta(\Delta - l\omega_0). \quad (25)$$

This result is identical to that obtained from the generating function method of Kubo⁴³ and Lax⁴⁴ for a single mode.^{18,42} We can extend this in the high-temperature limit, $\beta \gg \omega_0$, to

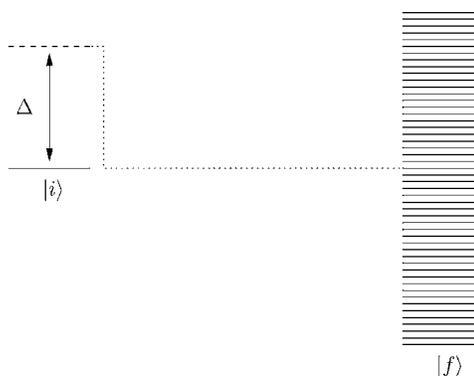


FIG. 3. Reaction exoergicity Δ in electron transfer is equivalent to an applied voltage with profile given by the dotted line.

the Marcus expression for ET rate. First, the delta function is rewritten,

$$\delta(\Delta - l\omega_0) = \frac{1}{\omega_0} \delta\left(\frac{\Delta}{\omega_0} - l\right), \quad (26)$$

and we set $l = \Delta/\omega_0$ and drop the delta function,¹⁸

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar\omega_0} |H_{if}|^2 e^{-S(2N_B+1) + \Delta\beta/2} I_{\Delta/\omega_0} [2S\sqrt{N_B(N_B+1)}]. \quad (27)$$

Making use of an asymptotic expression for the Bessel function,³⁶

$$I_l(z) \approx \frac{\exp(z - l^2/2z)}{\sqrt{2\pi z}}, \quad (28)$$

and approximate forms of the high-temperature Bose function, it can be shown¹⁸ that Eq. (27) simplifies to

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} |H_{if}|^2 \frac{\exp[-\beta/4\lambda(\Delta - \lambda)^2]}{\sqrt{4\pi\lambda/\beta}}, \quad (29)$$

where we have defined the Marcus reorganization energy λ in Equation (5). Equation (29) is the oftseen Marcus equation, which can be extended from the FGR to a two-mode case, as shown by Jortner,⁴² by redefining λ as a sum of individual mode contributions. The effects of distorted and displaced harmonic oscillators⁴⁵ as well as anharmonic effects^{46,47} can be treated within this same framework, although the appropriate polaron transformation will be much more taxing than the equivalent overlap integral calculation within the FGR.

In summary, we have outlined the formal connection between the steady-state current and the ET rate. After canonical transformation of the Hamiltonian and renormalization of the electronic Green's function, we began with the Landauer equation [Eq. (14)] and transformed to a rate equation in the golden rule regime [Eq. (20)]. Next, the rate expressions for zero temperature [Eq. (23)] and finite temperature [Eq. (25)] were derived. Finally in the high-temperature limit, the Marcus expression was recovered in Eq. (29).

Although we have carried out an extensive analysis of the electron-phonon interaction, the primary motivation for making use of the NEGF formalism in the calculation of ET rates is not to handle the Franck-Condon overlap factors, which are straightforwardly found in the FGR treatments, but rather to consider the effects of electron-electron interaction on the ET event. Treating both strong electron-electron and electron-phonon interactions will be a difficult challenge, but significant progress can be made in the regime of strong electron-phonon interaction and electron-electron interaction in the perturbative regime. Making use of the results of diagrammatic perturbation theory will allow for new formal progress in treating dynamical aspects of many-electron effects.

Another direction which we are currently investigating is the use of the NEGF methodology to explore explicitly the time dynamics involved in ET. This requires explicit consideration of both the transient and stationary terms in the cur-

rent, something that could show interesting connections with recent work using time-dependent density functional theory.^{48,49}

The authors thank Michael Galperin, Abraham Nitzan, and Robert Cave for helpful discussions. One of the authors (S.Y.) is grateful for support from the Office of Naval Research through a NDSEG fellowship. Funding was provided by the NSF/MRSEC program and by the MURI/DURINT program of the DoD.

¹V. Mujica, M. Kemp, and M. A. Ratner, J. Chem. Phys. **101**, 6849 (1994).

²V. Mujica, M. Kemp, and M. A. Ratner, J. Chem. Phys. **101**, 6856 (1994).

³X. Y. Zhu, Surf. Sci. Rep. **56**, 1 (2004).

⁴D. M. Adams, L. Brus, C. E. Chidsey, *et al.*, J. Phys. Chem. B **107**, 6668 (2003).

⁵A. Nitzan, Annu. Rev. Phys. Chem. **52**, 681 (2001).

⁶Y. Dahnovsky, J. Chem. Phys. **122**, 044501 (2005).

⁷Y. Dahnovsky, Phys. Rev. B **73**, 144303 (2006).

⁸N. S. Wingreen, K. W. Jacobsen, and J. W. Wilkins, Phys. Rev. B **40**, 11834 (1989).

⁹A. Nitzan, J. Phys. Chem. A **105**, 2677 (2001).

¹⁰M. Galperin (unpublished).

¹¹K. Walczak, Cent. Eur. J. Phys. **4**, 8 (2006).

¹²A. M. Kuznetsov and J. Ulstrup, J. Chem. Phys. **116**, 2149 (2002).

¹³T. Fujikawa, J. Phys. Soc. Jpn. **65**, 87 (1996).

¹⁴T. Fujikawa, J. Phys. Soc. Jpn. **68**, 2444 (1999).

¹⁵T. Fujikawa, J. Synchrotron Radiat. **8**, 76 (2001).

¹⁶H. Nakamura and K. Yamashita, J. Chem. Phys. **122**, 194706 (2005).

¹⁷J. Creechley and Y. Dahnovsky, Chem. Phys. **296**, 171 (2004).

¹⁸D. DeVault, *Quantum-Mechanical Tunnelling in Biological Systems* (Cambridge University Press, Cambridge, 1984).

¹⁹R. A. Marcus, J. Chem. Phys. **24**, 966 (1956).

²⁰R. A. Marcus, Annu. Rev. Phys. Chem. **15**, 155 (1964).

²¹S. Lakshmi, A. Datta, and S. K. Pati, Phys. Rev. B **72**, 045131 (2005).

²²T. Pacher, L. S. Cederbaum, and H. Koppel, J. Chem. Phys. **89**, 7367 (1988).

²³M. Braga, A. Broo, and S. Larsson, Chem. Phys. **156**, 1 (1991).

²⁴R. J. Cave and M. D. Newton, Chem. Phys. Lett. **249**, 15 (1996).

²⁵I. V. Kurnikov and D. N. Beratan, J. Chem. Phys. **105**, 9561 (1996).

²⁶A. A. Stuchebrukhov, J. Chem. Phys. **104**, 8424 (1996).

²⁷O. V. Prezhdo, J. T. Kindt, and J. C. Tully, J. Chem. Phys. **111**, 7818 (1999).

²⁸Q. Wu and T. Van Voorhis, J. Chem. Phys. **125**, 164105 (2006).

²⁹S. Datta, *Quantum Transport: Atom to Transistor* (Cambridge University Press, Cambridge, 2005).

³⁰I. G. Lang and Y. A. Firsov, Sov. Phys. JETP **16**, 1301 (1963).

³¹G. D. Mahan, *Many-Particle Physics* (Plenum Press, New York, 1983).

³²H. Haug and A. P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductors* (Springer, Berlin, 1996).

³³A. C. Hewson and D. Meyer, J. Phys.: Condens. Matter **14**, 427 (2002).

³⁴U. Lundin and R. H. McKenzie, Phys. Rev. B **66**, 075303 (2002).

³⁵M. Galperin, A. Nitzan, and M. A. Ratner, Phys. Rev. Lett. **96**, 166803 (2006).

³⁶G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, Cambridge, 1966).

³⁷When electron interaction is included, the full inelastic current equation will have to be used. For simplicity and to derive the Marcus result, we only treat the elastic case.

³⁸Y. Meir and N. S. Wingreen, Phys. Rev. Lett. **68**, 2512 (1992).

³⁹R. Landauer, IBM J. Res. Dev. **1**, 223 (1957).

⁴⁰R. Landauer, Philos. Mag. **21**, 863 (1970).

⁴¹See for example, G. C. Schatz and M. A. Ratner, *Quantum Mechanics in Chemistry*, 2nd ed. (Dover Publications, Inc., Mineola, New York, 2002), Chap. 4.

⁴²J. Jortner, J. Chem. Phys. **64**, 4860 (1976).

⁴³R. Kubo, Phys. Rev. **86**, 929 (1952).

⁴⁴M. Lax, J. Chem. Phys. **20**, 1752 (1952).

⁴⁵T. Kakitani and H. Kakitani, *Biochim. Biophys. Acta* **635**, 498 (1981).

⁴⁶N. C. Søndergaard, J. Ulstrup, and J. Jortner, *Chem. Phys.* **17**, 417 (1976).

⁴⁷S. Yeganeh and M. A. Ratner, *J. Chem. Phys.* **124**, 044108 (2006).

⁴⁸C. F. Craig, W. R. Duncan, and O. V. Prezhdo, *Phys. Rev. Lett.* **95**, 163001 (2005).

⁴⁹B. F. Habenicht, C. F. Craig, and O. V. Prezhdo, *Phys. Rev. Lett.* **96**, 187401 (2006).