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# Nuclear Dynamics at Molecule–Metal Interfaces: A Pseudoparticle Perspective

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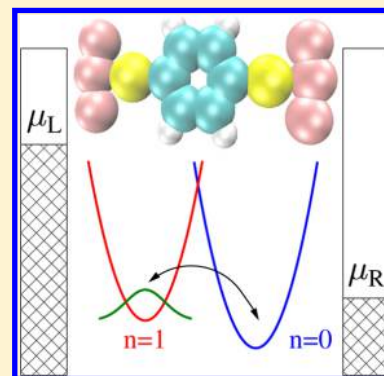
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## S Supporting Information

**ABSTRACT:** We discuss nuclear dynamics at molecule–metal interfaces including nonequilibrium molecular junctions. Starting from the many-body states (pseudoparticle) formulation of the molecule–metal system in the molecular vibronic basis, we introduce gradient expansion to reduce the adiabatic nuclear dynamics (that is, nuclear dynamics on a single molecular potential surface) into its semiclassical form while maintaining the effect of the nonadiabatic electronic transitions between different molecular charge states. This yields a set of equations for the nuclear dynamics in the presence of these nonadiabatic transitions, which reproduce the surface-hopping formulation in the limit of small metal–molecule coupling (where broadening of the molecular energy levels can be disregarded) and Ehrenfest dynamics (motion on the potential of mean force) when information on the different charging states is traced out.



The coupled electronic–nuclear dynamics in molecules positioned at and interacting with metal interfaces presents a fundamental problem that stems from the fact that in such systems the usual time scale separation between electron and nuclear dynamics does not necessarily hold. The problem has gained renewed interest in the context of nuclear dynamics in molecular conduction junctions, a presently active field of research because of its fundamental and practical importance.<sup>1–5</sup> Experimental measurements of inelastic electron tunneling spectroscopy,<sup>6–10</sup> and more recently fluorescence<sup>11–14</sup> and Raman<sup>15–19</sup> spectroscopies, serve as tools capable of providing information on the presence of the molecule in the junction and extent of heating of the device. Descriptions of transport,<sup>20</sup> heating,<sup>21</sup> instabilities,<sup>22,23</sup> and current (and light) induced chemistry<sup>4,24,25</sup> in junctions often require quantum-mechanical description beyond the Born–Oppenheimer approximation.

In junctions, electron transition events between molecule and contacts result in coupling between different adiabatic potential surfaces, resulting in nonadiabatic molecular dynamics (NAMD). NAMD plays an important role in many chemical dynamics processes, ranging from surface chemistry to spectroscopy, radiationless electronic relaxation, photochemistry, and electron transfer.<sup>26</sup> Considerations of nonadiabaticity are particularly important for molecules that exchange electrons with metal or semiconductor substrates because the rate of this exchange can be smaller or larger than characteristic nuclear time scales. Consequently, NAMD can drastically influence the response of molecular junctions and can dominate the transport behavior associated with many interesting phenomena ranging from current-induced chemistry to molecular motors.<sup>24,27</sup>

Full quantum-mechanical solution of electron–nuclear dynamics is possible only for relatively small systems.<sup>28,29</sup> Thus, one has to rely on quasiclassical formulations.<sup>30,31</sup> Among them, Ehrenfest dynamics<sup>32–35</sup> and fewest switches surface-hopping (SH) algorithm<sup>36,37</sup> are employed most often. The latter was applied to many problems in the gas phase,<sup>38–41</sup> and recently also to molecules near metallic surfaces.<sup>26,42–47</sup> From a theoretical perspective, the Ehrenfest method can be obtained as an expansion around the stationary (classical) solution of the quantum electron–nuclei problem.<sup>32,35</sup> Originally the SH algorithm was formulated in an ad hoc manner.<sup>36</sup> Later work has discussed its relation to the quantum–classical Liouville equation.<sup>48–50</sup> Such considerations are not readily suitable for molecule–metal systems that are characterized by exchange of electrons between a molecule and an electronic continuum as well as broadening of the molecular levels. Here we focus on this type of system.

In the absence of molecule–metal interaction, the molecule is presented in terms of its many-body molecular states that are usually described within the Born–Oppenheimer (BO) approximation. The latter is based on the assumption that nuclei are slow relative to the electronic dynamics. In the other extreme limit of strong molecule–metal interaction, where the molecule–metal electron exchange is also fast relative to the nuclear dynamics, the BO approximation is set with respect to hybrid molecule–metal electronic states.<sup>51</sup>

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In the intermediate situation of weak but nonvanishing molecule–metal electron exchange coupling, the BO approximation breaks down and the system dynamics includes transitions between electronic states of different charges that take place on the time scale of the nuclear dynamics. The ensuing dynamics can be described, e.g., in the basis of the BO states of the isolated molecule. (Note in passing that alternatively exact states of the molecular system<sup>52</sup> can be used as a basis.) So far the equations of motion (EOMs) used to describe the mixed quantum–classical dynamics have been postulated rather than derived. Here we offer a systematic derivation of the EOMs for such systems and discuss their relation to the SH algorithm. In doing this we provide, for the first time, a theoretical basis for the SH method as a limiting case of an exact EOM. Previous studies<sup>44–47</sup> are obtained from our consideration as a limiting case of an equilibrium junction with extremely weak molecule–metal coupling.

We start from the usual representation of the whole system (molecule plus contacts) where both electron ( $e$ ) and nuclear ( $n$ ) dynamics are taken into account. The Hamiltonian is

$$\hat{H}(r, R) = \hat{T}_n(R) + \hat{V}_{nn}(R) + \hat{T}_e(r) + \hat{V}_{ee}(r) + \hat{V}_{en}(r, R) \quad (1)$$

where  $r$  and  $R$  stand for the coordinates of all electrons and all nuclei in the system, respectively.  $\hat{T}_n$  ( $\hat{T}_e$ ) is the kinetic energy of the nuclei (electrons) and  $\hat{V}_{nn}$  ( $\hat{V}_{ee}$ ) is the Coulomb interaction between nuclei (electrons), while  $\hat{V}_{en}$  is the electron–nuclear attraction. Explicit expressions are

$$\hat{T}_n(R) = -\sum_{a=1}^{N_a} \frac{\Delta_{\vec{R}_a}}{2M_a}; \quad \hat{V}_{nn}(R) = \sum_{a<b}^{N_a} \frac{Z_a Z_b}{|\vec{R}_a - \vec{R}_b|} \quad (2)$$

$$\hat{T}_e(r) = -\sum_{i=1}^{N_e} \frac{\Delta_{\vec{r}_i}}{2}; \quad \hat{V}_{ee}(r) = \sum_{i<j}^{N_e} \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (3)$$

$$\hat{V}_{en}(r, R) = -\sum_{a=1}^{N_a} \sum_{i=1}^{N_e} \frac{Z_a}{|\vec{r}_i - \vec{R}_a|} \quad (4)$$

Here  $N_a$  and  $N_e$  represent the total numbers of atoms and electrons in the system, respectively. Here and below we have utilized atomic units, i.e.,  $m_e = k_b = \hbar = 1$ .

Our goal is to describe electronic and nuclear dynamics in a model junction that consists of a molecule,  $M$ , coupled to a number of metallic contacts,  $K$ . The latter are free electron reservoirs each at its own equilibrium. To do so we (artificially) separate the whole system into molecular and contacts parts and assume that their electronic structure has been determined. Nuclear dynamics is assumed to be confined to the molecular region only (and from now on we reserve  $R$  to represent the coordinates of the molecular atoms) with the contact atoms treated as static. Coupling between molecule and contacts is taken (as usual) to be single-particle operator (i.e., electron–electron interaction between electrons in  $M$  and  $K$  is disregarded). Below we take the index  $k$  to indicate both the band and the wave vector of an electron in  $K$  and use the second quantized representation of these states. The molecular subsystem will be treated in the language of vibronic states, which can be expanded in the basis of Born–Oppenheimer states<sup>53</sup>

$$\Phi_{ev}(r, R) = \psi_e(r, R) \chi_v^e(R) \equiv |ev\rangle \quad (5)$$

This yields the junction Hamiltonian in a mixed representation, where the molecule is described in terms of its vibronic states while the contacts are represented in the single-electron second quantized form

$$\hat{H} = \hat{H}_M + \sum_K (\hat{H}_K + \hat{V}_K) \quad (6)$$

$$\hat{H}_M = \sum_{\substack{e_1 v_1 \\ e_2 v_2}} H_{e_1 v_1, e_2 v_2}^M \hat{X}_{e_1 v_1, e_2 v_2} \quad (7)$$

$$\hat{H}_K = \sum_{k \in K} \epsilon_k \hat{c}_k^\dagger \hat{c}_k \quad (8)$$

$$\hat{V}_K = \sum_{k \in K} \sum_{\substack{e_1 v_1 \\ e_2 v_2}} V_{k, (e_1 v_1, e_2 v_2)}^K \hat{c}_k^\dagger \hat{X}_{e_1 v_1, e_2 v_2} + H.c. \quad (9)$$

where  $\hat{c}_k^\dagger$  ( $\hat{c}_k$ ) creates (annihilates) an electron in level  $k$  of the contacts,  $\hat{X}_{e_1 v_1, e_2 v_2} \equiv |e_1 v_1\rangle \langle e_2 v_2|$  is the molecular Hubbard (projection) operator,  $H_{e_1 v_1, e_2 v_2}^M \equiv \langle e_1 v_1 | \hat{H}_M | e_2 v_2 \rangle$ , and  $V_{k, (e_1 v_1, e_2 v_2)}^K \equiv \sum_{i=1}^{N_{e_2}} \int dr_M \int dR \psi_k^*(\vec{r}_i) \Phi_{e_1 v_1}^*(r \setminus \vec{r}_i, R) \hat{O}_1(r, R) \Phi_{e_2 v_2}(r, R)$  are matrix elements for the molecular Hamiltonian and coupling to contact  $K$ , respectively. [We note that (similar to the second quantization) information on antisymmetry of the electronic wave function enters via anticommutation relations of quasiparticle operators  $\hat{c}_k$  and Hubbard operators  $\hat{X}_{e_1 v_1, e_2 v_2}$ .] Here  $\int dr_M \dots$  integrates over electrons on the molecule;  $N_{e_2}$  is the number of electrons in the state  $|e_2 v_2\rangle$ ;  $\Phi_{e_1 v_1}(r \setminus \vec{r}_i, R)$  indicates vibronic state  $|e_1 v_1\rangle$  with one electron,  $\vec{r}_i$ , less than in the state  $|e_2 v_2\rangle$ ; and  $\hat{O}_1(r, R)$  is a single-electron operator, which (depending on the problem) can include contributions from eq 3 or 4.

Evaluating the dynamics of systems described by Hamiltonians of the type of eq 6 in terms of the many-body states of the isolated system, the nonequilibrium atomic limit,<sup>54</sup> can be treated within a number of techniques. Among them are the generalized quantum master equation (QME),<sup>55–61</sup> projection operator,<sup>62</sup> Hubbard<sup>63–68</sup> and PP<sup>28,69–75</sup> NEGF formulations, numerically exact renormalization group approaches,<sup>76–80</sup> and quantum Monte Carlo methodologies.<sup>29,81–85</sup> The latter are usually too heavy to be utilized in realistic simulations. We stress that within the nonequilibrium atomic limit<sup>54</sup> all the intramolecular interactions are taken into account exactly.

Here we use the PP-NEGF methodology in the lowest-order (noncrossing) approximation (NCA) (see the Supporting Information for details). We note that generalization to higher orders is straightforward.<sup>70</sup> The PP-NEGF formulation is based on the introduction of second quantization in the space of the many-body molecular states  $|ev\rangle = \hat{p}_{ev}^\dagger |0\rangle$ , where  $|0\rangle$  is vacuum state. The creation,  $\hat{p}_{ev}^\dagger$ , and annihilation,  $\hat{p}_{ev}$ , operators satisfy the usual commutation relations of either Fermi or Bose operators depending on the number of electrons in the state  $|ev\rangle$ . This formulation generates an extended Hilbert space, in which the physical subspace is defined by the normalization condition  $\sum_{ev} \hat{p}_{ev}^\dagger \hat{p}_{ev} = 1$ . The dynamical evolution of the system is expressed in terms of the pseudoparticle Green function, defined on the Keldysh contour as

$$G_{e_1 v_1, e_2 v_2}(\tau_1, \tau_2) \equiv -i \langle T_c \hat{p}_{e_1 v_1}^\dagger(\tau_1) \hat{p}_{e_2 v_2}(\tau_2) \rangle \quad (10)$$

where  $T_c$  is the contour ordering operator and  $\tau_{1,2}$  are the contour variables. It is convenient to represent this Green function (GF) in a different basis as

$$G_{e_1, e_2}(R_1, \tau_1; R_2, \tau_2) \equiv \sum_{\nu_1, \nu_2} \chi_{\nu_1}^{e_1}(R_1) G_{e_1 \nu_1, e_2 \nu_2}(\tau_1, \tau_2) \chi_{\nu_2}^{e_2}(R_2) \quad (11)$$

where  $\chi_{\nu}^{e_i}(R)$  is the vibrational wave function of the BO approximation (eq 5) in the isolated molecule. The retarded projection of GF (eq 11),  $G_{e_1, e_2}^r(R_1, \tau_1; R_2, \tau_2)$ , gives information on the many-body spectral function of the system

$$A_{e_1, e_2}(R_1, t_1; R_2, t_2) \equiv i[G_{e_1, e_2}^r(R_1, t_1; R_2, t_2) - G_{e_1, e_2}^a(R_1, t_1; R_2, t_2)] \quad (12)$$

where  $G_{e_1, e_2}^a(R_1, t_1; R_2, t_2) \equiv [G_{e_2, e_1}^r(R_2, t_2; R_1, t_1)]^*$ , while its lesser projection,  $G_{e_1, e_2}^<(R_1, t_1; R_2, t_2)$ , contains information on non-equilibrium distribution in the many-body states space of the molecule. These projections satisfy the usual Dyson equation (see the Supporting Information for details).<sup>75</sup>

Assuming slow nuclear dynamics relative to characteristic times of the electronic part of the system and/or bath, we perform first-order gradient expansion with respect to time and nuclear coordinates, keeping the electronic dynamics as purely quantum. Utilizing the PP-NEGF allows us to keep information on the potential energy surface while going to quasiclassical description of the nuclear motion. Note that the gradient expansion accounts approximately for the nuclear coordinates dependence of the molecular Hamiltonian and for the molecule–contact coupling. Such approximation is correct when the restoration of the electronic system–bath coherence (a purely electronic dynamics property) is much faster than nonstationary behavior in the system (a purely nuclear dynamics property). The corresponding time scales are defined by characteristic relaxation times in the system and the bath given (among other parameters) by the electron escape rate ( $\Gamma$ ) and bath temperature ( $T$ ), respectively. The expansion is legitimate when the inverse of either of these parameters is much smaller than the characteristic time scale of nuclear motion. Thus, the procedure provides description of surface hopping in the presence of finite molecule–metal coupling ( $\Gamma$ ). In the limit of extremely weak coupling (i.e., when  $\Gamma \rightarrow 0$ ), the expansion still holds at high temperatures.

Following the standard procedure,<sup>86</sup> we transfer to the Wigner variables, introducing slow (classical) coordinates and time  $R = (R_1 + R_2)/2$ ,  $t = (t_1 + t_2)/2$  and fast (quantum) variables  $R_q = R_1 - R_2$ ,  $t_q = t_1 - t_2$ , so that  $f(R_1, t_1; R_2, t_2) \rightarrow f(R, t; R_q, t_q)$  ( $f$  is an arbitrary correlation function), and perform Fourier transform in the latter

$$f_w(R, t; p, E) \equiv \int dR_q \int dt_q \exp(-ipR_q + iEt_q) f(R, t; R_q, t_q) \quad (13)$$

Performing first-order gradient expansion in the Dyson EOMs for lesser and retarded projections of GF (eq 11) leads to the following (see the Supporting Information for details of the derivations and explicit expressions; in energy resolved expressions for Green function projections we drop subscript “w” that would otherwise denote “Wigner transform”):

$$\begin{aligned} \frac{\partial}{\partial t} G_{e_1, e_2}^<(R, t; p, E) &= -i \sum_{e_3, e_4} \hat{\mathcal{L}}_{e_1, e_2; e_3, e_4}(R, p) G_{e_3, e_4}^<(R, t; p, E) \\ &- \sum_{e_3, e_4} \int dR' \int dp' \int \frac{dE'}{2\pi} \sum_K \hat{\mathcal{D}}_{e_1, e_2; e_3, e_4}^K(R, R', t; p, p', E, E') \\ &G_{e_3, e_4}^<(R', t; p', E') \end{aligned} \quad (14)$$

$$\begin{aligned} \sum_{e_3, e_4} (\hat{\mathcal{M}}_{e_1, e_2; e_3, e_4}(R, p, E) - \sum_K \hat{\mathcal{S}}_{e_1, e_2; e_3, e_4}^K(R, t; p, E)) \\ G_{e_3, e_4}^r(R, t; p, E) = \delta_{e_1, e_2} \end{aligned} \quad (15)$$

where  $\hat{\mathcal{L}}_{e_1, e_2; e_3, e_4}(R, p)$  and  $\hat{\mathcal{M}}_{e_1, e_2; e_3, e_4}(R, p, E)$  are the Liouvillian and free evolution superoperators (the latter term have been referred to as mass superoperator<sup>87</sup>), and  $\hat{\mathcal{D}}_{e_1, e_2; e_3, e_4}^K(R, R', t; p, p', E, E')$  and  $\hat{\mathcal{S}}_{e_1, e_2; e_3, e_4}^K(R, t; p, E)$  are the dissipation superoperators due to coupling to contact K. Equation 14 describes evolution of energy-resolved probability to find nuclei at positions  $R$  with momenta  $p$  at time  $t$  when electronic subsystem is characterized by the  $e_1, e_2$  element of the density matrix. Equation 15 describes evolution of the many-body spectral function, eq 12, which defines the dissipation superoperators in the EOMs. Equations 14 and 15 are the main final results.

To demonstrate relation to previous work we now consider a simple model of the molecule represented by single level linearly coupled to a single harmonic oscillator. There are only two electronic states in this problem,  $|0\rangle$  and  $|1\rangle$ , corresponding to empty and occupied level, respectively. The matrix representing the molecular Hamiltonian becomes in this case

$$H_{e_1, e_2}^M(R) = \delta_{e_1, e_2} \left( -\frac{1}{2} \frac{\partial^2}{\partial R^2} + U_{e_1}(R) \right) \quad (16)$$

where  $U_{e_1}(R) = \frac{R^2}{2} + \delta_{e_1, 1}(\varepsilon + \lambda R)$ . Here  $\varepsilon$  is the position of the electronic level and  $\lambda$  characterizes the strength of coupling between the electron and molecular vibration (harmonic oscillator).

We are interested in energy-resolved joint probabilities to observe the oscillator at point  $R$  with momentum  $p$  while the electron level is empty,  $P_0(R, t; p, E)$ , or occupied,  $P_1(R, t; p, E)$ . These probabilities are defined as

$$\begin{aligned} P_0(R, t; p, E) &\equiv +iG_{00}^<(R, t; p, E); \\ P_1(R, t; p, E) &\equiv -iG_{11}^<(R, t; p, E) \end{aligned} \quad (17)$$

Then we get from eq 14

$$\begin{aligned} \left( \frac{\partial}{\partial t} + p \frac{\partial}{\partial R} - R \frac{\partial}{\partial p} \right) P_0(R, t; p, E_0) \\ = \sum_K \int \frac{dE_1}{2\pi} \Gamma_K ([1 - f_K(E_{10})] A_0(R; p, E_0) P_1(R, t; p, E_1) \\ - f_K(E_{10}) A_1(R; p, E_1) P_0(R, t; p, E_0)) \end{aligned} \quad (18)$$

$$\begin{aligned} \left( \frac{\partial}{\partial t} + p \frac{\partial}{\partial R} - (R + \lambda) \frac{\partial}{\partial p} \right) P_1(R, t; p, E_1) \\ = \sum_K \int \frac{dE_0}{2\pi} \Gamma_K (f_K(E_{10}) A_1(R; p, E_1) P_0(R, t; p, E_0) \\ - [1 - f_K(E_{10})] A_0(R; p, E_0) P_1(R, t; p, E_1)) \end{aligned} \quad (19)$$

Here  $E_e$  ( $e = 0,1$ ) is the Fourier transform variable which corresponds to the energy of vibronic state  $e$ , i.e., electronic energy plus energy of the (now classical) nuclei ( $p^2/2m + R^2/2 + \delta_{e,1}(\varepsilon + \lambda R)$ );  $E_{10} \equiv E_1 - E_0$ ,  $f_K(E) = [e^{\beta_K(E-\mu_K)} + 1]^{-1}$  is the Fermi–Dirac thermal distribution in contact  $K$ ;  $\Gamma_K(E) \equiv 2\pi \sum_{k \in K} |V_k|^2 \delta(E - \varepsilon_k)$  is the electron escape rate to contact  $K$  (the wide band approximation, in which  $\Gamma_K$  is energy independent, is assumed); and  $A_e(R; p, E) = -2 \text{Im} G_{ee}^r(R; p, E)$  ( $e = 0,1$ ) is the many-body spectral function of the system, eq 12.

Similarly, from eq 15 we get ( $e = 0,1$ )

$$G_{ee}^r(R; p, E) = [E - \frac{p^2}{2} - U_e(R) - \Sigma_{ee}^r(R; p, E)]^{-1} \quad (20)$$

with

$$\Sigma_{00}^r(R; p, E_0) = -\frac{i}{2} \sum_K \Gamma_K \int \frac{dE_1}{2\pi} f_K(E_{10}) G_{11}^r(R; p, E_1) \quad (21)$$

$$\begin{aligned} \Sigma_{11}^r(R; p, E_1) \\ = -\frac{i}{2} \sum_K \Gamma_K \int \frac{dE_0}{2\pi} [1 - f_K(E_{10})] G_{00}^r(R; p, E_0) \end{aligned} \quad (22)$$

Now we compare our results, eqs 18–20, with previous considerations: (a) In the limit of extremely weak molecule–contacts coupling ( $\Gamma \rightarrow 0$ ), when  $\Sigma_{ee}^r \rightarrow -i0^+$ , we have from eqs 12 and 20  $A_e(R; p, E) \equiv -2 \text{Im} G_{ee}^r(R; p, E) \xrightarrow{\Gamma \rightarrow 0} 2\pi \delta(E - p^2/2 - U_e(R))$ . Then expressions 18 and 19 reduce to those discussed in ref 47. Thus, our study generalizes consideration of refs 44–47 by rigorously taking into account molecule–contacts hybridization. It also yields an expression applicable in the nonequilibrium realm of molecular junctions. (b) When the molecule metal coupling is relatively strong, the electron exchange is fast relative to the characteristic nuclear dynamics. In this case the individual molecular electronic states cannot be probed and only the sum of their probabilities is meaningful. It is easy to see that summing eqs 18 and 19 and integrating over corresponding energies we recover the Ehrenfest dynamics.

In conclusion, we have presented a derivation of expressions for nonadiabatic molecular dynamics in junctions starting from the full quantum-mechanical problem, thus providing a theoretical basis for the surface-hopping practice. The derivation starts from the exact EOMs for the pseudoparticle Green functions, describing the junction's response in the language of many-body (vibronic) states of an isolated molecule. Gradient expansion effectively separates semiclassical nuclear from quantum electron dynamics, yielding a Fokker–Planck type equation which incorporates both optical (intramolecular) and charge-transfer electron transitions as sources of nonadiabatic dynamics in junctions. The resulting equation can be viewed as the precursor of the SH algorithm. We show that the SH procedure described in refs 44–47 corresponds to the limit of negligible molecule–contacts coupling (the broadening was added a posteriori in an ad hoc manner). We also show that tracing out information on adiabatic surfaces leads to Ehrenfest dynamics (motion on the potential of mean force). Our study extends previous consideration by rigorously accounting for molecular hybridization with contacts and by introducing formulation capable of implementing the surface-hopping algorithm in a current-carrying (bias-induced)

molecular junction. At equilibrium and in the limit of weak molecule–contacts coupling our results reduce to those of ref 47. Thus, we provide for the first time a theoretical basis for the surface-hopping method as a limiting case of an exact EOM.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.5b02331.

Details of derivations for eqs 14 and 15 as well as discussion of the NCA (PDF)

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### Notes

The authors declare no competing financial interest.

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