The Journal of Chemical Physics

Erratum: "Surface hopping with a manifold of electronic states. III. Transients, broadening and the Marcus picture" [J. Chem. Phys. 142, 234106 (2015)]

Cite as: J. Chem. Phys. **143**, 189902 (2015); https://doi.org/10.1063/1.4935713
Submitted: 02 November 2015 • Accepted: 02 November 2015 • Published Online: 11 November 2015

Wenjie Dou, Abraham Nitzan and Joseph E. Subotnik

Erratum: "Surface hopping with a manifold of electronic states. III. Transients, broadening and the Marcus picture" [J. Chem. Phys. 142, 234106 (2015)]

Wenjie Dou,[1] Abraham Nitzan,[2] and Joseph E. Subotnik[1]
[1]*Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA*
[2]*School of Chemistry, The Sackler Faculty of Science, Tel Aviv University, Tel Aviv 69978, Israel*

(Received 2 November 2015; accepted 2 November 2015; published online 11 November 2015)

[http://dx.doi.org/10.1063/1.4935713]

An error appeared in Eqs. (22) and (23) for the referenced article. As originally published, the equations of motion for the reduced density matrices are lacking their respective complex conjugates.[1] The correct nonsecular (full) quantum master equation (nQME) should read

$$\begin{aligned}\frac{d\rho_0(i,j)}{dt} &= -\frac{\mathbf{i}}{\hbar}(\epsilon_0(i)-\epsilon_0(j))\rho_0(i,j) - \frac{\Gamma}{2\hbar}\sum_{i',k} f(\epsilon_1(i')-\epsilon_0(k))F_{i\to i'}F_{k\to i'}\rho_0(k,j)\\ &\quad - \frac{\Gamma}{2\hbar}\sum_{i',k}\rho_0(i,k)f(\epsilon_1(i')-\epsilon_0(k))F_{j\to i'}F_{k\to i'} + \frac{\Gamma}{2\hbar}\sum_{i',j'}(1-f(\epsilon_1(j')-\epsilon_0(j)))F_{i\to i'}F_{j\to j'}\rho_1(i',j')\\ &\quad + \frac{\Gamma}{2\hbar}\sum_{i',j'}\rho_1(i',j')(1-f(\epsilon_1(i')-\epsilon_0(i)))F_{i\to i'}F_{j\to j'}, \qquad (22)\\ \frac{d\rho_1(i',j')}{dt} &= -\frac{\mathbf{i}}{\hbar}(\epsilon_1(i')-\epsilon_1(j'))\rho_1(i',j') - \frac{\Gamma}{2\hbar}\sum_{i,k'}(1-f(\epsilon_1(k')-\epsilon_0(i)))F_{i\to i'}F_{i\to k'}\rho_1(k',j')\\ &\quad - \frac{\Gamma}{2\hbar}\sum_{i,k'}\rho_1(i',k')(1-f(\epsilon_1(k')-\epsilon_0(i)))F_{i\to j'}F_{i\to k'} + \frac{\Gamma}{2\hbar}\sum_{i,j} f(\epsilon_1(j')-\epsilon_0(j))F_{i\to i'}F_{j\to j'}\rho_0(i,j)\\ &\quad + \frac{\Gamma}{2\hbar}\sum_{i,j}\rho_0(i,j)f(\epsilon_1(i')-\epsilon_0(i))F_{i\to i'}F_{j\to j'}. \qquad (23)\end{aligned}$$

For the sake of clarity, above, we use bold **i** to denote the imaginary unit. As a result of this error, the nQME data in Figures 1 and 2 of the reference paper are only slightly changed, as presented below. The overall conclusions of our paper are

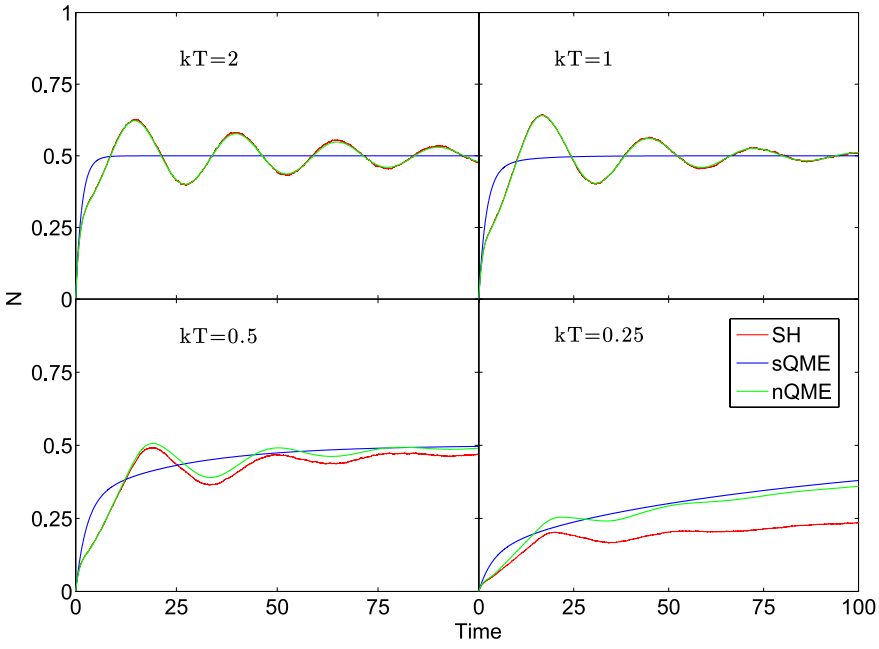

FIG. 1. Transient dynamics: the impurity electron population as a function of time. $\Gamma = 1$, $\hbar\omega = 0.3$, e-ph coupling $g = 0.75$, $\bar{E}_d = 0$. Note that SH and nQME agree at high temperatures. The sQME does not show any oscillations in electronic population, whereas the nQME shows transient oscillations which are (empirically) close to the frequency ω. At time zero, the phonon is prepared to be equilibrated thermally (assuming the impurity is unoccupied).

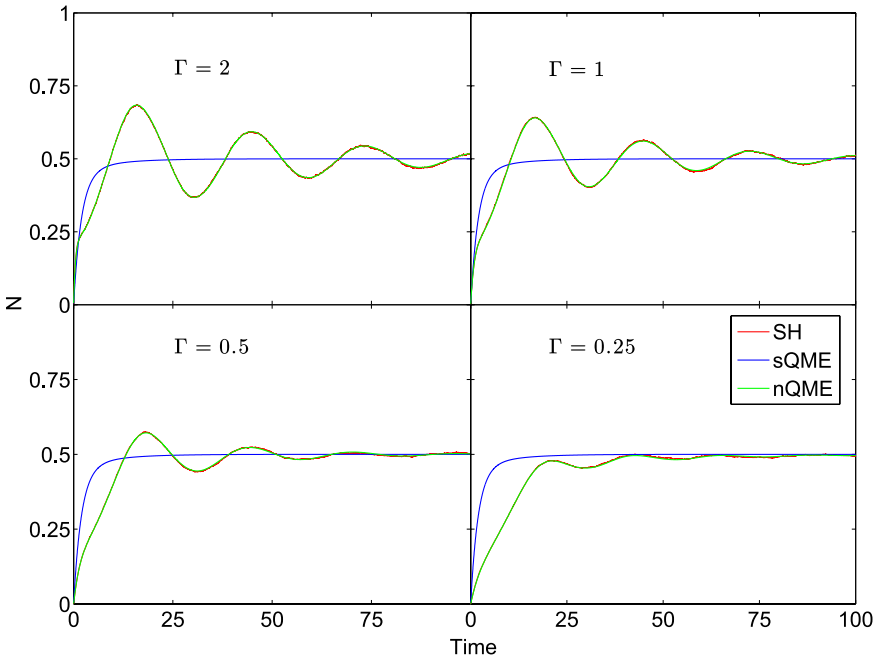

FIG. 2. Transient dynamics: the impurity electron population as a function of time. $kT = 1$, $\hbar\omega = 0.3$, e-ph coupling $g = 0.75$, $\bar{E}_d = 0$. Note that SH and nQME agree over a large range of Γ. The sQME does not show any oscillations in electronic population, whereas the nQME shows transient oscillations which are (empirically) close to the frequency ω. At time zero, the phonon is prepared to be equilibrated thermally (assuming the impurity is unoccupied).

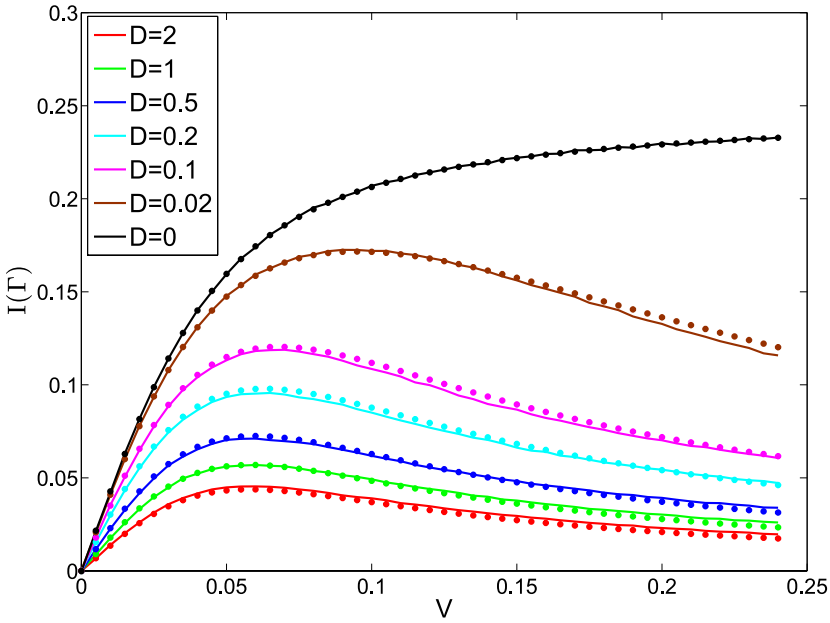

FIG. 6. I-V curves for different values of D (see Eq. (46)). Lines from SH, dots from the sQME. $g = 0.005$, $\hbar\omega = 0.003$, $kT = 0.01$, $\Gamma = 2\Gamma_0 = 0.01$, $\bar{E}_d = 0$. We observe negative differential resistance when D is nonzero.

unchanged; in fact, however, it now appears that the classical master equation matches up with the nonsecular quantum master equation even better than before.

There was also a typo in Eq. (26) of the referenced article, which should read

$$F_{i\to i'} = (p!/Q!)^{1/2}\lambda^{Q-p}e^{-\lambda^2/2}L_p^{Q-p}(\lambda^2)[\mathrm{sgn}(i'-i)]^{i-i'}. \tag{26}$$

Additionally, there was a numerical error for Figure 6 for the secular quantum master equation (sQME) data. After correction, sQME agrees with surface hopping (SH) almost exactly.

[1]W. Dou, A. Nitzan, and J. E. Subotnik, "Surface hopping with a manifold of electronic states. III. Transients, broadening and the Marcus picture," J. Chem. Phys. **142**, 234106 (2015).