# Supplementary Material for "Exact Potential Energy Surface for Molecules in Cavities"

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## I. EXACT FACTORIZATION EQUATIONS

The full equations of the EF factorization we use here are based on the generalization given in Ref. [1] of the original time-dependent EF equations of Ref. [2, 3]. These are based on the factorization

$$\Psi(\underline{\underline{r}},\underline{\underline{q}},\underline{\underline{R}},t)=\chi(\underline{\underline{R}},t)\Phi_{\underline{\underline{R}}}(\underline{\underline{r}},\underline{\underline{q}},t) \tag{1}$$

where $\underline{\underline{r}}$, $\underline{\underline{q}}$, $\underline{\underline{R}}$ represent all electronic-, photonic displacement-field mode-, and nuclear- coordinates, respectively, and the partial normalization condition

$$\int |\Phi_{\underline{\underline{R}}}(\underline{\underline{r}},\underline{\underline{q}},t)|^2 d\underline{\underline{r}}d\underline{\underline{q}}=1 \tag{2}$$

is satisfied. The marginal and conditional parts each satisfy the following coupled equations of motion:

$$\left(\hat{H}_{\rm BO}+\hat{H}_p+\hat{V}_{pm}+\hat{V}_{\rm dipSE}+\hat{U}_{\rm ep-n}-\epsilon(\underline{\underline{R}},t)\right)\Phi_{\underline{\underline{R}}}(\underline{\underline{r}},\underline{\underline{q}},t)=i\partial_t\Phi_{\underline{\underline{R}}}(\underline{\underline{r}},\underline{\underline{q}},t) \tag{3}$$

$$\left(\sum_{J=1}^{N_n}(-i\nabla_J+\mathbf{A}_J(\underline{\underline{R}},t))^2/2M_J+\epsilon(\underline{\underline{R}},t)\right)\chi(\underline{\underline{R}},t)=i\partial_t\chi(\underline{\underline{R}},t) \tag{4}$$

with

$$\hat{U}_{ep-n}=\sum_{J=1}^{N_n}\frac{1}{M_J}\left(\frac{(-i\nabla_J-\mathbf{A}_J(\underline{\underline{R}},t))^2}{2}+\left(\frac{-i\nabla_J\chi(\underline{\underline{R}},t)}{\chi(\underline{\underline{R}},t)}+\mathbf{A}_J(\underline{\underline{R}},t)\right)\cdot\left(-i\nabla_J-\mathbf{A}_J(\underline{\underline{R}},t)\right)\right) \tag{5}$$

$$\epsilon(\underline{\underline{R}},t)=\langle\Phi_{\underline{\underline{R}}}|\hat{H}_{\rm BO}+\hat{H}_p+\hat{V}_{pm}+\hat{V}_{\rm dipSE}+\hat{U}_{\rm ep-n}-i\partial_t|\Phi_{\underline{\underline{R}}}\rangle_{\underline{\underline{r}},\underline{\underline{q}}} \tag{6}$$

$$\mathbf{A}_J(\underline{\underline{R}},t)=\langle\Phi_{\underline{\underline{R}}}|-i\nabla_J\Phi_{\underline{\underline{R}}}\rangle_{\underline{\underline{r}},\underline{\underline{q}}} \tag{7}$$

and all other terms in Eqs. 3 and 4 are given in the main text for the one-dimensional model we studied. The notation $\langle...\rangle_{\underline{\underline{r}},\underline{\underline{q}}}$ indicates an integral over all photonic displacement-field and electronic coordinates only.

The marginal part, $\chi(\underline{\underline{R}},t)$ is a nuclear wavefunction in the sense that it reproduces the exact nuclear density and exact nuclear current-density of the exact full photon-matter wavefunction. The equations 3–7 are form-invariant under the phase-transformation $\Phi_{\underline{\underline{r}},\underline{\underline{q}}}(\underline{\underline{R}},t)\rightarrow\Phi_{\underline{\underline{r}},\underline{\underline{q}}}(\underline{\underline{R}},t)e^{i\theta(\underline{\underline{R}},t)}$, $\chi(\underline{\underline{R}},t)\rightarrow\chi(\underline{\underline{R}},t)e^{-i\theta(\underline{\underline{R}},t)}$ with the potentials undergoing the gauge-like transformation $\mathbf{A}_J(\underline{\underline{R}},t)\rightarrow\mathbf{A}_J(\underline{\underline{R}},t)+\nabla_J\theta(\underline{\underline{R}},t)$, $\epsilon(\underline{\underline{R}},t)\rightarrow\epsilon(\underline{\underline{R}},t)+\partial_t\theta(\underline{\underline{R}},t)$, and the factorization Eq. 1 is unique up to such a transformation.

The model we studied has a one-dimensional nuclear coordinate so a gauge can always be found in which the vector potential $\mathbf{A}(\underline{\underline{R}},t)$ is zero. This is the gauge we chose in our calculations. The equations then simplify in the sense, for example, that there is only one potential, the scalar $\epsilon(\underline{\underline{R}},t)$ appearing in the nuclear equation, and the scalar potential can then be written as three terms, as prescribed in Eqs. (6)–(9) of the main paper.

In practise, we obtained the potential energy surface $\epsilon(\underline{\underline{R}},t)$ by inversion [3]. That is, we first solved the time-dependent Schrödinger equation for $\Psi(r,q,R,t)$ on a three-dimensional grid, and extracted $\chi(R,t)=|\chi(R,t)|e^{iS(R,t)}$ using

$$|\chi(R,t)|=\sqrt{\int dqdr|\Psi(r,q,R,t)|^2} \tag{8}$$

and

$$S(R,t)=\int^R\left(\frac{\mathrm{Im}\int drdq\,\Psi(r,q,R',t)\frac{d\Psi(r,q,R',t)}{dR'}}{|\chi(R',t)|^2}\right)dR' \tag{9}$$

Then we found $\Phi_{r,q}(R,t)=\Psi(r,q,R,t)/\chi(R,t)$ enabling us to evaluate the matrix elements involved for $\epsilon(R,t)$ (Eqs.(6) – (9) of the main text).

## II. NUMERICAL DETAILS

In our calculations, we used 192, 96, 1280 points on a grid of size $\pm120.20$ a.u., $\pm80$ a.u., $\pm9.5$ a.u., for the electronic, photonic or nuclear calculation respectively. We also used a time-step of $0.1$ a.u.

## III. MOVIES

We provide three movies:

(i) **movieCpl0p005** shows the dynamics for the case where the resonant frequency of the cavity is $\omega_\alpha = 0.1$au and the coupling strength is $\lambda = 0.005$ in red, compared to the cavity-free dynamics in black.

Top left: exact TDPES, shown against the background of polaritonic surfaces in blue and green, and the nuclear density, scaled by 0.1 and shifted down, is shown in the lower part of all plots in the first row.

Top middle: weighted polaritonic component of the exact TDPES $\epsilon_{\rm wpol}(R,t)$ .

Right middle: gauge-dependent component of the exact TDPES $\epsilon_{\rm GD}(R,t)$.

Lower left: BO coefficients $C_i(R,t)$ as defined in Eq. (11) of the main text as a function of time

Lower middle: number of photons emitted as a function of time

Lower right: electronic (solid) and nuclear (dashed) dipole moments as a function of time.

(ii) **movieCpl0p001** as above but for coupling strength $\lambda = 0.001$.

(iii) **movieCpl0p005phdenCBO** shows the $n$-photon resolved densities and BO-coefficients for the $\omega_\alpha = 0.1$ and $\lambda = 0.005$ case as compared with the cavity-free case.

Top left panel: the total nuclear density (as a reference)

Top right panel: the $0$-photon resolved density

Middle left: the $1$-photon resolved density

Middle right: the $2$-photon resolved density

Lower left: the BO coefficients in the cavity

Lower right: the BO-coefficients for the cavity-free case.


[1] N. M. Hoffmann, H. Appel, A. Rubio, and N. T. Maitra, The European Physical Journal B **91**, 180 (2018).

[2] A. Abedi, N. T. Maitra, and E. K. U. Gross, Phys. Rev. Lett. **105**, 123002 (2010).

[3] A. Abedi, N. T. Maitra, and E. K. U. Gross, J. Chem. Phys. **137**, 22A530 (2012).