

Supplementary Material

The Ehrenfest method with Fully Quantum Nuclear Motion (Qu-Eh): Application to Charge Migration in Radical Cations

Andrew J. Jenkins¹, K. Eryn Spinlove², Morgane Vacher³, Graham A. Worth² and Michael A Robb⁴

1) Dept. of Chemistry, University of Washington, Seattle, WA 98195, USA

2) Dept. of Chemistry, University College London, 20, Gordon St., WC1H 0AJ, UK

3) Dept. of Chemistry-Ångström, Uppsala University, Lägerhyddsvägen 1, 751 21 Uppsala, Sweden

4) Dept. of Chemistry, Imperial College London, London SW7 2AZ, United Kingdom

Energy Derivatives and the Hamiltonian in the LHA approximation

In the following development we assume mass-scaled coordinates and atomic units. We now give the expressions for the Hamiltonian matrix elements for the gwp (equation (S1)). We begin with expression for the gwp:

$$g_i(\mathbf{q}, t) = \prod_{\alpha} (2\pi\sigma_{\alpha}^2)^{-1/4} \exp\left(-\frac{1}{4\sigma_{\alpha}^2} [q_{\alpha} - q_{i\alpha}(t)]^2 + ip_{i\alpha}(t)q_{\alpha}\right) \quad (\text{S1})$$

Using a local harmonic approximation of the Ehrenfest potential (equation 55 main text), the nuclear Hamiltonian matrix elements read:

$$\frac{H_{ij}^N}{S_{ij}} = V(\mathbf{q}^j) + \sum_{\alpha} \left[\frac{1}{8\sigma_{\alpha}^2} + \left(\frac{q_{i\alpha} - q_{j\alpha}}{2} - i\sigma_{\alpha}^2(p_{i\alpha} - p_{j\alpha}) \right) G_{\alpha}^j \right. \\ \left. + \frac{1}{2} \left(\frac{p_{i\alpha} + p_{j\alpha}}{2} + i \frac{q_{i\alpha} - q_{j\alpha}}{4\sigma_{\alpha}^2} \right)^2 \right. \\ \left. + \frac{1}{2} \sum_{\beta} H_{\alpha\beta}^j \left(\sigma_{\alpha}^2 \delta_{\alpha\beta} + \left(\frac{q_{i\alpha} - q_{j\alpha}}{2} - i\sigma_{\alpha}^2(p_{i\alpha} - p_{j\alpha}) \right) \left(\frac{q_{i\beta} - q_{j\beta}}{2} - i\sigma_{\beta}^2(p_{i\beta} - p_{j\beta}) \right) \right) \right] \quad (\text{S2})$$

The derivatives are given as

$$\begin{aligned}
\frac{H_{ij}^{N(q_{i\alpha}0)}}{S_{ij}} = & \left(\frac{q_{j\alpha} - q_{i\alpha}}{4\sigma_{\alpha}^2} - i \frac{p_{i\alpha} - p_{j\alpha}}{2} \right) \frac{H_{ij}^N}{S_{ij}} \\
& + \frac{1}{2} \left[G_{\alpha}^j + \sum_{\beta} H_{\alpha\beta}^j \left(\frac{q_{i\beta} - q_{j\beta}}{2} - i\sigma_{\beta}^2 (p_{i\beta} - p_{j\beta}) \right) \right] \\
& + \frac{i}{4\sigma_{\alpha}^2} \left(\frac{p_{i\alpha} + p_{j\alpha}}{2} + i \frac{q_{i\alpha} - q_{j\alpha}}{4\sigma_{\alpha}^2} \right)
\end{aligned}
\tag{S3}$$

and

$$\begin{aligned}
\frac{H_{ij}^{N(p_{i\alpha}0)}}{S_{ij}} = & -i \left(\frac{q_{i\alpha} + q_{j\alpha}}{2} - i\sigma_{\alpha}^2 (p_{i\alpha} - p_{j\alpha}) \right) \frac{H_{ij}^N}{S_{ij}} \\
& - i\sigma_{\alpha}^2 \left[G_{\alpha}^j + \sum_{\beta} H_{\alpha\beta}^j \left(\frac{q_{i\beta} - q_{j\beta}}{2} - i\sigma_{\beta}^2 (p_{i\beta} - p_{j\beta}) \right) \right] \\
& + \frac{1}{2} \left(\frac{p_{i\alpha} + p_{j\alpha}}{2} + i \frac{q_{i\alpha} - q_{j\alpha}}{4\sigma_{\alpha}^2} \right)
\end{aligned}
\tag{S4}$$

The above equations (S2-S4) make use of the first and second derivatives of the energy with respect to the geometrical parameters, as expressed in equation 57 in the main text.

Thanks to the work of Almlöf and Taylor¹ the analytical derivatives have been presented systematically for a CASSCF wavefunction. The general expressions (equation 57 main text) are given in equations S5 and S6. As discussed in the main text we have three types of variables and derivatives: $\mathbf{X}$, the orthogonal rotation of the orbitals among themselves as one displaces the geometry with the derivative $\mathbf{X}_{\alpha}$ with respect to the nuclear co-ordinate α ; $\mathbf{C}$, the orthogonal rotation of the CI eigenvectors among

themselves as one displaces the geometry with the derivative C_α with respect to the nuclear co-ordinate; and Y , the re-orthogonalization of the orbitals as one displaces the geometry with the derivative S_α .

The gradient then involves E^C , the gradient of the energy with respect to the rotation of the CI eigenvectors, E^X the gradient of the energy with respect to the rotation of the orbitals and E^Y the gradient of the energy with respect to the re-orthogonalization of the orbitals. The leading term in the gradient E^α is the gradient of the energy due to the change in the molecular Hamiltonian with nuclear geometry (the Hellmann-Feynman term). The gradient¹ is given compactly in equation S5 below. The second derivatives have the general form given in equation S6, where the notation is the same as in equation 56, e.g. E^{C_α} is the mixed second derivative with respect to CI vector rotation and nuclear displacement. Note that S_α in equations S5 and S6 is the derivative overlap matrix. Quantities such as X_α have to be obtained from the coupled perturbed equations which have to be solved for each nuclear displacement. These equations are similar to the CASSCF coupled perturbed equations² except that the CI vector rotation coefficients correspond to rotations between the Ehrenfest vector and its orthogonal complement.

$$G_\alpha = E^\alpha + E^C C_\alpha + E^X X_\alpha - \frac{1}{2} E^Y S_\alpha \quad (S5)$$

$$\begin{aligned} H_{\alpha,\beta} = & E^{\alpha,\beta} + E^C C_{\alpha,\beta} + E^{C_\alpha} C_\beta + E^{C_\beta} C_\alpha + E^{CC} C_\alpha C_\beta + E^{CX} C_\alpha X_\beta - \frac{1}{2} E^{CY} C_\alpha S_\beta \\ & + E^X X_{\alpha,\beta} + E^{X_\alpha} X_\beta + E^{X_\beta} X_\alpha + E^{XX} X_\alpha X_\beta + E^{XC} X_\alpha C_\beta - \frac{1}{2} E^{XY} X_\alpha S_\beta - \frac{1}{2} E^{Y_\alpha} S_\beta \\ & - \frac{1}{2} E^{Y_\beta} S_\alpha + \frac{1}{2} E^Y S_\alpha S_\beta - \frac{1}{2} E^Y S_{\alpha,\beta} + \frac{1}{4} E^{YY} S_\alpha S_\beta - \frac{1}{2} E^{YC} S_\alpha C_\beta - \frac{1}{2} E^{YX} S_\alpha X_\beta \end{aligned} \quad (S6)$$

1. J. Almlöf and P. R. Taylor, International Journal of Quantum Chemistry **27** (6), 743-768 (1985).

2. N. Yamamoto, T. Vreven, M. Robb, M. Frisch and H. Schlegel, Chem Phys Lett **250** (3-4), 373-378 (1996).