

Control defeasance by anti-alignment in the excited state

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I. SUPPLEMENTARY INFORMATION

Here we provide some details on the Hamiltonian model and Ehrenfest equations used in the manuscript.

As indicated, we use a two-dimensional model for a diatomic molecule with a single electron, where the in-plane electron motion is mediated by soft-core Coulomb interactions with the nuclei, V_{sc} , and the coupling with the field $\mathbf{E}(t)$, V_{int} , while the nuclear motion is affected by the gradient of the potential energy, evaluated as a Hellmann-Feynman force. Defining the laboratory-fixed Cartesian coordinates for the nuclei, $\tilde{X}_j^{(\alpha)}$ ($j = 1, 2$ for the X , Y components, $\alpha = a, b$ for the nuclei of mass M_α and charge Z_α) and equivalently the \tilde{x}_j laboratory-fixed Cartesian electron coordinates, collectively written as $\tilde{\mathbf{X}}$ and $\tilde{\mathbf{x}}$ respectively, the electronic degrees of freedom obey the time-dependent Schrödinger equation (TDSE)

$$i \frac{\partial}{\partial t} \psi(\tilde{\mathbf{x}}) = -\frac{1}{2} \sum_j \frac{\partial^2}{\partial \tilde{x}_j^2} \psi(\tilde{\mathbf{x}}) + (V_{sc} + V_{int}) \psi(\tilde{\mathbf{x}}) \quad (1)$$

where we use atomic units, and the soft-core Coulomb potential is

$$V_{sc} = -\sum_\alpha Z_\alpha \left[\sum_j \left(\tilde{x}_j - \tilde{X}_j^{(\alpha)}(t) \right)^2 + \epsilon^2 \right]^{-\frac{1}{2}} + Z_a Z_b \left[\sum_j \left(\tilde{X}_j^{(2)}(t) - \tilde{X}_j^{(1)}(t) \right)^2 \right]^{-1} \quad (2)$$

where we have chosen $\epsilon = 1/\sqrt{2}$. Although the model is general, in this work we will use linearly polarized external fields, $\mathbf{E} = \mathbf{i}E_1 + \mathbf{j}E_2$. Disregarding the effect of the magnetic field (although the charged cation is accelerating in the presence of the field), in the dipole approximation the interaction potential is given by

$$V_{int} = \sum_j E_j(t) \left(\tilde{x}_j - Z_b \tilde{X}_j^{(b)}(t) - Z_a \tilde{X}_j^{(a)}(t) \right) \quad (3)$$

On the other hand, the nuclear degrees of freedom under the Hellmann-Feynman force approximation obey Newton equations

$$\frac{d^2}{dt^2} \tilde{X}_j^{(\alpha)} = -\frac{1}{M_\alpha} \langle \psi(\tilde{\mathbf{x}}) \left| \frac{\partial (V_{sc} + V_{int})}{\partial \tilde{X}_j^{(\alpha)}} \right| \psi(\tilde{\mathbf{x}}) \rangle . \quad (4)$$

As the derivatives are analytic, the gradient is evaluated in close form. In this work both nuclei are protons, so $Z_\alpha = 1$ and $M_\alpha = M$.

It is convenient to decouple the internal and center of mass motion and work with coordinates relative to the center of mass, not only to reduce the number of variables, but mainly

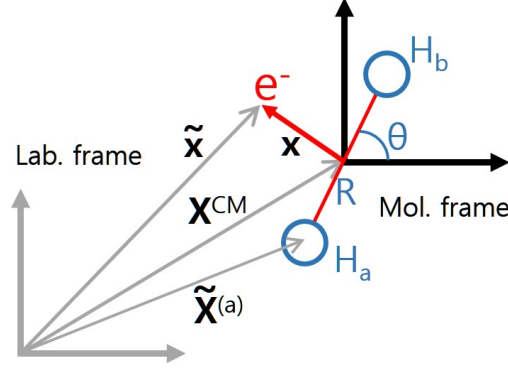


FIG. 1: Diagram showing the choice of coordinates used in the model

to avoid having to work with very large grids for the electronic coordinates, as the whole molecular cation moves in the gradient of the field. We first neglect the difference between the molecule's center of mass and the nuclear center of mass, $\mathbf{X}^{CM} = \sum_{\alpha} M_{\alpha} \tilde{\mathbf{X}} / \sum_{\alpha} M_{\alpha}$, and define the molecular frame Cartesian coordinates, as shown in the figure, $\mathbf{x} = \tilde{\mathbf{x}} - \mathbf{X}^{CM}$, $\mathbf{X} = \tilde{\mathbf{X}} - \mathbf{X}^{CM}$. Then V_{sc} is a function of \mathbf{x} and $\mathbf{X}(t)$, while $V_{int} = \mathbf{E}(t) (\mathbf{x} - \mathbf{X}^{CM})$, is a function of \mathbf{x} and $\mathbf{X}^{CM}(t)$. Now the equations for \mathbf{X} depend only on the gradient of V_{sc} , while those for \mathbf{X}^{CM} depend only on the gradient of V_{int} , which can be immediately integrated:

$$i \frac{\partial}{\partial t} \psi(\mathbf{x}) = -\frac{1}{2} \sum_j \frac{\partial^2}{\partial x_j^2} \psi(\mathbf{x}) + [V_{sc} + \mathbf{E}(t)\mathbf{x} - \mathbf{E}(t)\mathbf{X}^{CM}(t)] \psi(\mathbf{x}) \quad (5)$$

and

$$\frac{d^2}{dt^2} X_j^{(\alpha)}(t) = -\frac{1}{M_{\alpha}} \langle \psi(\mathbf{x}) \left| \frac{\partial V_{sc}}{\partial X_j^{(\alpha)}} \right| \psi(\mathbf{x}) \rangle, \quad (6)$$

$$\frac{d^2}{dt^2} \mathbf{X}^{CM}(t) = \frac{1}{4M} \mathbf{E}(t) \quad (7)$$

where, within the same level of approximation, we use the electron mass for the reduced mass of the system and neglect the mass-polarization term. In fact, in Eq.(5), the last term in the parenthesis can be taken away from the TDSE by a unitary transformation of the wave function, which receives a time-dependent phase due to the accelerated motion of the center of mass of the charged molecule in the presence of the field, $\varphi(t) = \int_0^t \mathbf{E}(t') \mathbf{X}^{CM}(t') dt'$, where $\mathbf{X}^{CM}(t)$ is obtained from the solution of Eq.(7).

The internal nuclear motion can be further expressed in polar variables, $X_1^{(a)} =$

$-r/2 \cos \theta$, $X_2^{(a)} = -r/2 \sin \theta$ ($X_j^{(b)} = -X_j^{(a)}$), such that

$$V_{sc} = - \left[\left(x + \frac{r}{2} \cos \theta \right)^2 + \left(y + \frac{r}{2} \sin \theta \right)^2 + \epsilon^2 \right]^{-1/2} - \left[\left(x - \frac{r}{2} \cos \theta \right)^2 + \left(y - \frac{r}{2} \sin \theta \right)^2 + \epsilon^2 \right]^{-1/2} + \frac{1}{r} \quad (8)$$

$\equiv V_1 + V_2 + r^{-1}$ and therefore,

$$\frac{d^2}{dt^2} r = \frac{1}{M} (V_1^3 - V_2^3) [\langle x \rangle \cos \theta + \langle y \rangle \sin \theta] + \frac{r}{2M} (V_1^3 + V_2^3) - \frac{2}{Mr^2} \quad (9)$$

$$\frac{d^2}{dt^2} \theta = \frac{1}{Mr} (V_1^3 - V_2^3) [\langle y \rangle \cos \theta - \langle x \rangle \sin \theta] \quad (10)$$

where $\langle x \rangle \equiv \langle \psi(\mathbf{x}) | x | \psi(\mathbf{x}) \rangle$ and $\langle y \rangle \equiv \langle \psi(\mathbf{x}) | y | \psi(\mathbf{x}) \rangle$ are the average electronic positions, obtained by integrating the electronic wave function in the grid.