

The role of anti-alignment in the dynamics of the excited states of molecules

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I. SUPPLEMENTARY INFORMATION

A. Derivation of Eq. (1)

The nuclear and electronic Hamiltonian, in atomic units, is given by

$$H = -\sum_i \frac{1}{2m_i} \nabla_i^2 + V(\mathbf{R}, \mathbf{r}) + E z^{\text{lab}} - E Z_a^{\text{lab}} - E Z_b^{\text{lab}}, \quad (\text{A.1})$$

where z^{lab} corresponds to the z coordinate of the position of the electron, Z_a^{lab} corresponds to the z coordinate of the position of the (a) nucleus, and Z_b^{lab} corresponds to the z coordinate of the position of (b) nucleus, all in the laboratory frame, \mathbf{r} the spatial coordinate of the electron relative to the geometric center of the nuclei (CGN), and \mathbf{R} the internuclear vector (pointing from the nucleus (b) to the nucleus (a)). We define the geometric center of the nuclei as the average of the nuclear positions, namely

$$\mathbf{R}_{\text{CGN}} = \frac{1}{2} \mathbf{R}_a^{\text{lab}} + \frac{1}{2} \mathbf{R}_b^{\text{lab}},$$

and the center of mass of the nuclei as

$$\mathbf{R}_{\text{CGN}} = \frac{m_a}{m_a + m_b} \mathbf{R}_a^{\text{lab}} + \frac{m_b}{m_a + m_b} \mathbf{R}_b^{\text{lab}},$$

where m_a is the mass of the (a) nucleus and m_b is the mass of the (b) nucleus.

Introducing into Eq. (A.1), the definition of the electronic coordinates with respect to the geometric center of the nuclei \mathbf{R}_{CGN}

$$\begin{aligned} \mathbf{r}^{\text{lab}} &= \mathbf{r} + \mathbf{R}_{\text{CGN}} \\ &= \mathbf{r} + \frac{m_b - m_a}{2(m_a + m_b)} \mathbf{R} + \mathbf{R}_{\text{CMN}}, \end{aligned}$$

and the definition of the nuclear positions with respect to the center of mass of the nuclei \mathbf{R}_{CMN}

$$\mathbf{R}_a^{\text{lab}} = +\frac{m_b}{m_a + m_b} \mathbf{R} + \mathbf{R}_{\text{CMN}},$$

and

$$\mathbf{R}_b^{\text{lab}} = -\frac{m_a}{m_a + m_b} \mathbf{R} + \mathbf{R}_{\text{CMN}}.$$

We obtain the following Hamiltonian, obviating the contribution of the position of nuclear center of mass (constant term),

$$H = -\frac{1}{2\mu_{ab}} \nabla_{\mathbf{R}}^2 - \frac{1}{2} \nabla_{\mathbf{r}}^2 + V(\mathbf{R}, \mathbf{r}) + E z - \frac{m_b - m_a}{2(m_a + m_b)} E R \cos \theta.$$

The corresponding Schrödinger equation is Eq. (1).

B. The prolate spheroidal treatment and the electronic basis

The electronic Hamiltonian is given by

$$H_e(R, \theta, E) = -\frac{1}{2}\nabla_{\mathbf{r}}^2 + V(\mathbf{R}, \mathbf{r}) + E z - \frac{1}{2}\alpha ER \cos \theta$$

with

$$V(\mathbf{R}, \mathbf{r}) = -\frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R},$$

where r_α is the distance between the electron and the nuclei α ($\alpha = a, b$). The position of the nuclei (a) and (b) are given by

$$\mathbf{R}_a = +\frac{1}{2}R(t) \sin \theta(t) \hat{x} + \frac{1}{2}R(t) \cos \theta(t) \hat{z}$$

and

$$\mathbf{R}_b = -\frac{1}{2}R(t) \sin \theta(t) \hat{x} - \frac{1}{2}R(t) \cos \theta(t) \hat{z},$$

with respect to the geometric center of the nuclei \mathbf{R}_{CGN} . To apply the prolate spheroidal treatment in its usual formulation, we require the nuclei to be over the \hat{z} axis. To ensure so, we make the following transformation

$$A = \frac{1}{R} \begin{pmatrix} \cos \theta & 0 & -\sin \theta \\ 0 & 1 & 0 \\ \sin \theta & 0 & \cos \theta \end{pmatrix}$$

over the electron and nuclear coordinates, which is a rotation and a contraction. So a vector \mathbf{v} in these new coordinates is $\tilde{\mathbf{v}} = A\mathbf{v}$. In this coordinates the position of the nuclei (a) and (b) are given by

$$\tilde{\mathbf{R}}_a = +\frac{1}{2}\hat{z}$$

and

$$\tilde{\mathbf{R}}_b = -\frac{1}{2}\hat{z},$$

respectively. So the nuclei are fixed in the \hat{z} axis. The Hamiltonian now reads

$$H_e(R, \theta, E) = -\frac{1}{2R^2}\nabla_{\tilde{\mathbf{r}}}^2 + \frac{1}{R}V(\tilde{\mathbf{R}}, \tilde{\mathbf{r}}) + ER(\tilde{z} \cos \theta - \tilde{x} \sin \theta) - \frac{1}{2}\alpha ER \cos \theta. \quad (\text{B.1})$$

Having done so, we now introduce the prolate spheroidal coordinates (λ, μ, ϕ) , where

$$\begin{aligned} \lambda &= |\tilde{\mathbf{r}} - \tilde{\mathbf{R}}_a| + |\tilde{\mathbf{r}} - \tilde{\mathbf{R}}_b|, \\ \mu &= |\tilde{\mathbf{r}} - \tilde{\mathbf{R}}_a| - |\tilde{\mathbf{r}} - \tilde{\mathbf{R}}_b|, \end{aligned}$$

and ϕ is the azimuthal angle. Note that $1 \leq \lambda \leq \infty$, $-1 \leq \mu \leq 1$, and $0 \leq \phi \leq 2\pi$. We need this coordinate system to allow us to write the Coulomb interaction as

$$\frac{1}{R}V(\tilde{\mathbf{r}}, \tilde{\mathbf{R}}(t)) = -\frac{4\lambda}{R(\lambda^2 - \mu^2)} + \frac{1}{R},$$

and since the volume element is $dV = (1/2)^3 R^3 (\lambda^2 - \mu^2) d\lambda d\mu d\phi$, the coordinates remove the singularities of the potential when projecting into a basis. The factor R^3 stands to compensate for the contraction of the coordinates. Note also that the overall electronic Hamiltonian in Eq. (B.1) is just a linear combination of operators, where the coefficients of this linear combination are functions of R and θ . Hence, we only need to calculate the matrix elements of these operators just once to find the matrix elements of the Hamiltonian for all configurations (values of R and θ).

Finally, we define the following basis,

$$\gamma_{\nu, \eta, m}(\lambda, \mu, \phi) = \frac{1}{\sqrt{2\pi}} u_{m, \nu}(\lambda) v_{m, \eta}(\mu) e^{im\phi}, \quad (\text{B.2})$$

with

$$u_{m, \nu}(\lambda) = N_{\nu}^m e^{-\alpha(\lambda-1)} (\lambda^2 - 1)^{|m|/2} L_{\nu-|m|}^{2|m|}(2\alpha(\lambda-1))$$

and

$$v_{m, \eta}(\mu) = M_{\eta}^m P_{\eta}^m(\mu).$$

Here $L_p^q(x)$ are the associated Legendre functions, $P_p^q(x)$ the associated Laguerre Polynomials,

$$N_{\nu}^m = \sqrt{(2\alpha)^{2|m|+1} \frac{(\nu - |m|)!}{(\nu + |m|)!}},$$

$$M_{\eta}^m = \sqrt{\left(\eta + \frac{1}{2}\right) \frac{(\eta - m)!}{(\eta + m)!}},$$

and $\alpha = e^{0.1i}$ is a complex parameter to represent outgoing waves, preventing unphysical reflections. The index m is the electron's angular momentum projection onto the \hat{z} axis. We also impose that $m = 0, \pm 1, \pm 2, \dots, \pm m_{\max}$, $\eta = |m|, |m| + 1, \dots, |m| + \mu_{\max}$, and $\nu = |m|, |m| + 1, \dots, |m| + \nu_{\max}$. So m_{\max} , μ_{\max} , and ν_{\max} are cutoff parameters that control the basis size.

As the reader may note, the previously defined basis is not orthogonal (see Eq. (B.2)). To obtain an orthonormal basis we solve for the eigenstates of the Hamiltonian $H_e(R, \theta, 0)$ without the field for $R = 2a_0$. By sorting the eigenstates by their energies, we can define

the orthonormal electronic basis $\{\psi_n\}_{n \in \mathbb{N}}$. This helps us to sparse the matrix elements of the Hamiltonian, reducing computational costs. In this way, one can define properly $\langle \psi_n | H_e | \psi_{n'} \rangle$ as a function of R and θ .

Finally, we must state that when applying the transformation A to the Schrodinger equation instead of the Hamiltonian, non-adiabatic terms arise. Our numerical calculations including or excluding these terms, show no appreciable difference in the analysis that we show in this work. We attribute this to the difference of mass between the proton and the electron. Consequently, we omit these terms to speed up our calculations in the present situation.