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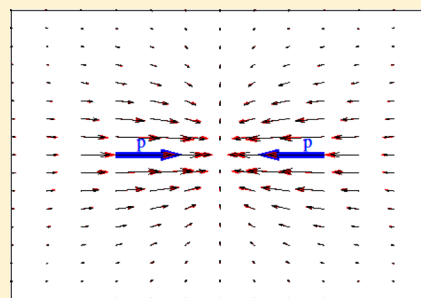
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ABSTRACT: A molecule in the electronic ground state described in the Born–Oppenheimer approximation (BOA) by the wave function $\Psi_{\text{BO}} = \Phi_0 \chi_0$ (where Φ_0 is the time-independent electronic energy eigenfunction and χ_0 is a time-dependent nuclear wave packet) exhibits a nonzero *nuclear* flux density, whereas it always displays zero *electronic* flux density (EFD), because the electrons are in a stationary state. A hierarchical approach to the computation of the EFD within the context of the BOA, which utilizes only standard techniques of quantum chemistry (to obtain Φ_0) and quantum dynamics (to describe the evolution of χ_0 on the ground-state potential energy surface), provides a resolution of this puzzling, nonintuitive result. The procedure is applied to H_2^+ oriented parallel with the z -axis and vibrating in the ground state $^2\Sigma_g^+$. First, Φ_0 and χ_0 are combined by the coupled-channels technique to give the normally dominant z -component of the EFD. Imposition of the constraints of electronic continuity, cylindrical symmetry of Φ_0 and two boundary conditions on the EFD through a scaling procedure yields an improved z -component, which is then used to compute the complementary orthogonal ρ -component. The resulting EFD agrees with its highly accurate counterpart furnished by a non-BOA treatment of the system.



1. INTRODUCTION

Many properties of electronically adiabatic processes that take place in the electronic ground state of a molecular system (e.g., electronic and nuclear population densities, fluxes, and yields (time-integrated fluxes), and also *nuclear flux densities*) can be adequately described within the framework of the Born–Oppenheimer approximation (BOA).^{1,2} However, a straightforward attempt to calculate the *electronic flux density* (EFD) (i.e., the expectation value $\langle \mathbf{j}_e(\mathbf{r}, t) \rangle$, where \mathbf{j}_e stands for the quantum observable) directly from the BOA wave function fails (i.e., the EFD is zero). The reason is that the BOA assumes that the light electrons adjust their motion instantly in response to the movement of the heavy nuclei. The electrons are therefore in a stationary state (i.e., an eigenstate of the electronic Hamiltonian) at all times. It has long been known that $\langle \mathbf{j}_e(\mathbf{r}, t) \rangle = \mathbf{0}$ for such a state.³

Alternative measures of electron flow in the electronic ground state that sidestep this conundrum are reviewed elsewhere.⁴ For the reader's convenience, we mention here several of the more relevant ones. Nafie has derived an expression for the EFD associated with vibronic transitions, which involves non-adiabatic couplings between electronic ground and excited states.⁵ The formula has been used to compute EFDs that accompany vibronic transitions in formaldehyde and ethylene.^{6,7} From a different perspective Patchkovskii has developed a “sum-of-states” (SOS) formula for the EFD equivalent to Nafie's formula and used it to generate EFDs associated with classical quasi-static movements of the nuclei in H_2 , butadiene, and the 7-azaindole complex.⁸ The SOS method consequently not only invokes nonadiabatic coupling but also neglects quantum effects of

dispersion and interference in the nuclear wave packet. Non-adiabatic coupling also plays a central role in the approach of Takatsuka and co-workers, who employ “non-adiabatic electron wave packet dynamics”, a procedure by which the EFD is computed along the classical trajectory of the nuclear configuration that evolves according to coupled quantum-classical equations of motion.^{9,10} They have used a particular version of this theory, namely the semiclassical Ehrenfest theory (SET), to generate EFDs associated with vibrating H_2 ,¹¹ the electron-transfer reaction $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$,¹¹ and proton transfer in the formic-acid dimer¹¹ and the phenol–ammonia complex.¹² They have also introduced a complex (i.e., nonreal) “time-shift flux” [density] that can be computed for electronically adiabatic states described in the BOA.¹¹ We remark finally that a nonvanishing EFD can be generated by preparing the molecule in a superposition of degenerate^{13,14} or near-degenerate^{15,16} electronic excited states.

The goal of the present article is to show that, despite the “traditional” failure of the BOA (i.e., the result of a straightforward computation is $\langle \mathbf{j}_{e,\text{BOA}}(\mathbf{r}, t) \rangle = \mathbf{0}$), one can employ standard methods of quantum chemistry and quantum dynamics within the context of the BOA to obtain an approximate nonzero EFD that agrees with the corresponding accurate EFD computed without the BOA. To demonstrate the approach, we examine H_2^+ oriented parallel with the z -axis and vibrating in the electronic ground state

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$^2\Sigma_g^+$, for which system an accurate EFD is readily obtainable. Indeed, an accurate EFD⁴ for this system was used previously as a benchmark in testing¹⁷ the coupled-channels (CC) theory,¹⁸ which provides the approximate z -component of the EFD ($\langle j_{ez,CC}(\mathbf{r},t) \rangle$) as a principal ingredient of the present calculation.

To reach our goal, we devise a hierarchical procedure that starts from the BOA and the CC theory. We observe that the accurate EFD ($\langle j_e(\mathbf{r},t) \rangle$) generally consists of a dominant z -component ($\langle j_{ez}(\mathbf{r},t) \rangle$) parallel with the internuclear axis and a weaker orthogonal ρ -component ($\langle j_{e\rho}(\mathbf{r},t) \rangle$). (We employ cylindrical coordinates $\mathbf{r} = (\rho, z, \varphi)$ and note that the φ -component is absent because of the cylindrical symmetry of the electronic ground state.) As shown previously,¹⁷ the CC scheme¹⁸ yields a reasonably good approximation ($\langle j_{ez,CC}(\mathbf{r},t) \rangle$) to the accurate z -component.⁴ We therefore use $\langle j_{ez,CC} \rangle$, together with the electronic probability density $d_{e,BO}$ computed from the BOA wave function, to calculate the ρ -component ($\langle j_{e\rho,CC} \rangle$). We note that the *exact* EFD obeys four constraints, to wit, electronic continuity (i.e., the components of the EFD must satisfy the electronic continuity equation), cylindrical symmetry, and two boundary conditions (i.e., that $\langle j_{e\rho} \rangle$ must vanish on the internuclear axis ($\rho = 0$) and (exponentially) as the distance ρ from the internuclear axis becomes very large). These constraints lead to an exact formula (eq 14 below) that expresses $\langle j_{e\rho} \rangle$ as “output” corresponding to $\langle j_{ez} \rangle$, plus the exact electronic probability density d_e as “input”. We enforce these same constraints on the approximate EFD by scaling the CC “input” $\langle j_{ez,CC} \rangle$ according to eq 16 below. Substitution of the expression for the scaled CC “input” $\langle j_{ez,SCC} \rangle$ into the exact formula yields a revised formula (eq 18 below) for the scaled “output” $\langle j_{e\rho,SCC} \rangle$. The final result of the hierarchical BOA \rightarrow CC \rightarrow SCC approach is the two-dimensional EFD vector field $\langle j_{e,SCC} \rangle = \langle j_{ez,SCC} \rangle \mathbf{e}_z + \langle j_{e\rho,SCC} \rangle \mathbf{e}_\rho$.

To perform the required numerical analysis, we represent all quantities discretely on a grid in the ρ - z plane. It is unfortunate, however, that the accurate EFD⁴ formerly employed as a reference is available only on a rather coarse grid that, for the present purpose, does not afford a sufficiently precise representation of one of the critical boundary conditions, namely the vanishing of the EFD on the internuclear axis. We therefore calculate a new accurate EFD on a fine grid, using a non-BOA wave function expressed as a linear combination of vibronic eigenstates of the *complete* Hamiltonian.¹⁹ The new accurate EFD agrees with the earlier one on the previous grid.⁴

2. THEORY AND COMPUTATIONS

We consider H_2^+ in the electronic ground state $^2\Sigma_g^+$ oriented so that the internuclear separation (\mathbf{R}) is parallel with the z -axis of the laboratory reference frame. We assume that the internal reference frame is parallel with the lab frame. Hence, the internal wave function is given in the BOA by

$$\Psi_{BO}(\mathbf{r}, R, t) = \Phi_0(\mathbf{r}; R) \chi_0(R, t) \quad (1)$$

where $\Phi_0(\mathbf{r}; R)$ is the (real) ground-state eigenfunction of the electronic Hamiltonian (with R fixed) and $\chi_0(R, t)$ is the (complex) wave packet governing the relative (internal) motion of the protons. In eq 1 \mathbf{r} stands for the position of the electron with respect to the nuclear center of mass (NCM) and t stands for time. Because Φ_0 is cylindrically symmetric, we represent the BOA wave function in terms of cylindrical coordinates [$\mathbf{r} = (\rho, z, \varphi)$] as $\Psi_{BO}(\rho, z, R, t) = \Phi_0(\rho, z; R) \chi_0(R, t)$ (i.e., Ψ_{BO} is independent of the azimuthal angle φ). (Note that ρ , which signifies the distance of the

electron from the z -axis replaces r , which is used in ref 17 to represent this quantity; here r has the significance of the distance of the electron from the NCM.) As in our previous studies,^{4,17} we take the initial wave function to be

$$\Psi_{BO}(\rho, z, R, 0) = \Phi_0(\rho, z; R) \chi_{0,0}(R - \bar{R}) \quad (2)$$

where $\chi_{0,0}(R - \bar{R})$ is the vibrational ground-state energy eigenfunction displaced by \bar{R} in the positive R direction. That is, the bond is initially *stretched* by the distance \bar{R} from its equilibrium length. As in the prior investigations,^{4,17} we put $\bar{R} = 2.00 a_0$. The BOA wave function is normalized according to

$$\begin{aligned} \int dR \int d\mathbf{r} |\Psi_{BO}(\mathbf{r}, R, t)|^2 \\ = \int_0^\infty dR \int_0^{2\pi} d\varphi \int_{-\infty}^\infty dz \int_0^\infty d\rho \rho [\Phi_0(\rho, z; R)]^2 |\chi_0(R, t)|^2 \\ = 1 \end{aligned} \quad (3)$$

An essential element of the CC theory is that each nucleus α has an associated electronic probability density Δ_α that depends on the nuclear configuration.¹⁸ Seeking an intuitively reasonable representation that allows a “natural” partitioning of the *total* electronic probability density among the nuclei, and that has the added virtue of being undergirded by the well developed infrastructure of quantum chemistry, we choose the LCAO MO theory to represent Φ_0 . Thus, Φ_0 is partitioned into contributions $\Phi_{0\alpha}$ associated with the two nuclei of H_2^+ according to

$$\Phi_0(\rho, z; R) = \sum_{\alpha=a,b} \Phi_{0\alpha}(\rho, z; R) \quad (4a)$$

where $\Phi_{0\alpha}$ is expressed in terms of the atomic orbitals (AOs) $\phi_{l\alpha}$ as

$$\Phi_{0\alpha}(\rho, z; R) \equiv \sum_{l_\alpha} c_{l_\alpha}(R) \phi_{l_\alpha}(\rho, z, R) \quad \alpha = a, b \quad (4b)$$

and $c_{l_\alpha}(R)$ is the coefficient of the l th AO centered on nucleus α . Then, for fixed R , the *time-independent* electronic probability density can be written in the BOA as

$$\tilde{d}_{e,BO}(\rho, z; R) \equiv [\Phi_0(\rho, z; R)]^2 = \sum_{\alpha=a,b} \Delta_\alpha(\rho, z; R) \quad (4c)$$

where

$$\Delta_\alpha(\rho, z; R) \equiv \Phi_0(\rho, z; R) \Phi_{0\alpha}(\rho, z; R) \quad \alpha = a, b \quad (4d)$$

Employing the MOLPRO software,²⁰ we compute Φ_0 and the ground-state potential energy curve $V_0(R)$ by the LCAO MO Hartree–Fock technique. The wave function is represented in the high-level aug-cc-pVTZ basis set. The vibrational ground-state wave function $\chi_{0,0}$ is calculated by means of the WAVEPACKET software²¹ on a grid of 256 points equally spaced at distance $\Delta R = 0.036328 a_0$ over the range $0.7 a_0 < R < 10.0 a_0$. The equilibrium internuclear separation is $R_e = 2.045 a_0$ and the minimum of $V_0(R)$ is $-0.6023 E_h$.

The nuclear wave packet $\chi_0(R, t)$ is propagated by means of the WAVEPACKET software²¹ on the same grid used for $\chi_{0,0}$ with a time-step size of $0.01523 \hbar/E_h$ (0.368 as). The (time-dependent) nuclear probability density is given by

$$d_{n,BO}(R, t) \equiv |\chi_0(R, t)|^2 \quad (5a)$$

and the *nuclear* probability flux density by

$$j_{n,BO}(R, t) \equiv \frac{\hbar}{2i\mu_n} \left[\chi_0^*(R, t) \frac{\partial \chi_0(R, t)}{\partial R} - \text{c.c.} \right] \quad (5b)$$

In eq 5b $\mu_n = M_p/2$, where M_p is the proton's mass; "c.c." signifies the complex conjugate of the preceding term in brackets. The norm of the nuclear wave function $\int_0^\infty dR \tilde{d}_{n,BO}(R,t)$ remains unity within a precision of 0.001%. Weighting $\tilde{d}_{e,BO}(\rho,z;R)$ by $d_{n,BO}(R,t)$ yields the *time-dependent* electronic probability density according to

$$d_{e,BO}(\rho,z,t) = \int_0^\infty dR \tilde{d}_{e,BO}(\rho,z;R) d_{n,BO}(R,t) \quad (6)$$

The CC EFD, which has only a z -component, is given by¹⁸

$$\begin{aligned} \langle j_{ez,CC}(\rho,z,t) \rangle &= \frac{1}{2} \int_0^\infty dR [\Delta_b(\rho,z;R) - \Delta_a(\rho,z;R)] j_{n,BO}(R,t) \\ &= \frac{1}{2} \int_0^\infty dR [\Delta_b(\rho,z;R) - \Delta_a(\rho,z;R)] j_{n,BO}(R,t) \end{aligned} \quad (7)$$

The observer, who is stationed on the NCM, sees an EFD that is the resultant of two components—one associated with nucleus b moving in one direction and the other associated with nucleus a moving in the opposite direction. The factor $1/2$ accounts for the fact that the velocity of either nucleus with respect to the NCM is one-half the relative velocity of the nuclei. The electronic probability density assigned to each nucleus is weighted by the nuclear flux density, because the nuclei are not localized. Both the $1/2$ -weighted nuclear flux density and the CC electronic probability density are thus defined in a coherent manner with respect to the same (i.e., the NCM) frame.

Having obtained the "input" ($\langle j_{ez,CC} \rangle$ and $d_{e,BO}$) to our hierarchical procedure, we proceed to determine the "output" ($\langle j_{ep,CC} \rangle$). We note that the cylindrical symmetry of the electronic state implies that the angular component of the EFD vanishes:

$$\langle j_{ep}(\rho,z,t) \rangle = \langle j_{ep,CC}(\rho,z,t) \rangle = 0 \quad (8)$$

The determination of the ρ -component exploits four constraints on the EFD. First, the EFD should obey the electronic continuity equation, which can be written as

$$\nabla \cdot \langle \mathbf{j}_e(\mathbf{r},t) \rangle + \partial d_e(\mathbf{r},t)/\partial t = 0 \quad (9)$$

for the *exact* electronic probability density and flux density, where

$$d_e(\mathbf{r},t) = \int_0^\infty dR |\Psi(\mathbf{r},R,t)|^2 \quad (10a)$$

$$\langle \mathbf{j}_e(\mathbf{r},t) \rangle = \frac{\hbar}{2i\mu_e} \int_0^\infty dR [\Psi^*(\mathbf{r},R,t) \nabla \Psi(\mathbf{r},R,t) - \text{c.c.}] \quad (10b)$$

$\mu_e \equiv 2m_e M_p/(m_e + 2M_p)$, and $\Psi(\mathbf{r},R,t)$ is the *exact* wave function. Second, because the φ -component of the EFD vanishes (eq 8), we can cast eq 9 in cylindrical coordinates as²²

$$\frac{1}{\rho} \frac{\partial [\rho \langle j_{ep}(\rho,z,t) \rangle]}{\partial \rho} = - \frac{\partial \langle j_{ez}(\rho,z,t) \rangle}{\partial z} - \frac{\partial d_e(\rho,z,t)}{\partial t} \quad (11)$$

Multiplying eq 11 by ρ , fixing z and t , and integrating from 0 to ρ , we get

$$\begin{aligned} \rho \langle j_{ep}(\rho,z,t) \rangle &= g(z,t) - \int_0^\rho d\rho' \rho' \left[\frac{\partial \langle j_{ez}(\rho',z,t) \rangle}{\partial z} + \frac{\partial d_e(\rho',z,t)}{\partial t} \right] \\ &= g(z,t) - \int_0^\rho d\rho' \rho' \left[\frac{\partial \langle j_{ez}(\rho',z,t) \rangle}{\partial z} + \frac{\partial d_e(\rho',z,t)}{\partial t} \right] \end{aligned} \quad (12)$$

where $g(z,t)$ may depend on z and t . Third, the boundary condition

$$\lim_{\rho \rightarrow 0} \langle j_{ep}(\rho,z,t) \rangle = 0 \quad (13)$$

implies that $g(z,t) = 0$. Hence from eqs 12 and 13 we obtain

$$\begin{aligned} \langle j_{ep}(\rho,z,t) \rangle &= -\rho^{-1} \int_0^\rho d\rho' \rho' \left\{ \frac{\partial \langle j_{ez}(\rho',z,t) \rangle}{\partial z} + \frac{\partial d_e(\rho',z,t)}{\partial t} \right\} \\ &= -\rho^{-1} \int_0^\rho d\rho' \rho' \left\{ \frac{\partial \langle j_{ez}(\rho',z,t) \rangle}{\partial z} + \frac{\partial d_e(\rho',z,t)}{\partial t} \right\} \end{aligned} \quad (14)$$

Fourth, we have the boundary condition

$$\begin{aligned} \lim_{\rho \rightarrow \infty} \rho \langle j_{ep}(\rho,z,t) \rangle &= -\lim_{\rho \rightarrow \infty} \int_0^\rho d\rho' \rho' \left\{ \frac{\partial \langle j_{ez}(\rho',z,t) \rangle}{\partial z} + \frac{\partial d_e(\rho',z,t)}{\partial t} \right\} = 0 \\ &= -\lim_{\rho \rightarrow \infty} \int_0^\rho d\rho' \rho' \left\{ \frac{\partial \langle j_{ez}(\rho',z,t) \rangle}{\partial z} + \frac{\partial d_e(\rho',z,t)}{\partial t} \right\} = 0 \end{aligned} \quad (15)$$

These four constraints (eqs 8, 11, 13, and 15) should apply as well to the approximate EFD. To enforce them, we scale the CC z -component of the EFD according to

$$\langle j_{ez,SCC}(\rho,z,t) \rangle \equiv \int_0^z dz' \lambda(z',t) \frac{\partial \langle j_{ez,CC}(\rho,z',t) \rangle}{\partial z'} \quad (16)$$

where the scaling (S) factor is given by

$$\lambda(z,t) \equiv - \frac{\int_0^\infty d\rho \rho \frac{\partial d_{e,BO}(\rho,z,t)}{\partial t}}{\int_0^\infty d\rho \rho \frac{\partial \langle j_{ez,CC}(\rho,z,t) \rangle}{\partial z}} \quad (17)$$

Note that the formula in eq 16 satisfies the condition $\langle j_{ez,SCC}(\rho,0,t) \rangle = 0$ due to the symmetry of the system (i.e., the z -component of the EFD vanishes in the plane $z = 0$). Substituting eq 16 into eq 14, we obtain the scaled CC ρ -component of the EFD:

$$\begin{aligned} \langle j_{ep,SCC}(\rho,z,t) \rangle &= -\rho^{-1} \int_0^\rho d\rho' \rho' \left\{ \frac{\partial \langle j_{ez,SCC}(\rho',z,t) \rangle}{\partial z} + \frac{\partial d_{e,BO}(\rho',z,t)}{\partial t} \right\} \\ &= -\rho^{-1} \int_0^\rho d\rho' \rho' \left\{ \lambda(z,t) \frac{\partial \langle j_{ez,CC}(\rho',z,t) \rangle}{\partial z} + \frac{\partial d_{e,BO}(\rho',z,t)}{\partial t} \right\} \end{aligned} \quad (18)$$

Observe that the scaling defined by eq 17 is constructed so that both the z - and ρ -components of the resulting SCC EFD satisfy all required physical constraints, namely, the electronic continuity eq 9 and the two boundary conditions specified by eqs 13 and 15. In contrast, the unscaled (i.e., $\lambda(z,t) = 1$) CC results in a ρ -component that satisfies eqs 9 and 13, but not eq 15. In summary, the SCC z - and ρ -components, given respectively by eqs 16 and 18, constitute the two-dimensional EFD vector field produced by the BOA \rightarrow CC \rightarrow SCC hierarchy:

$$\langle \mathbf{j}_{e,SCC}(\rho,z,t) \rangle = \langle j_{ez,SCC}(\rho,z,t) \rangle \mathbf{e}_z + \langle j_{ep,SCC}(\rho,z,t) \rangle \mathbf{e}_\rho \quad (19)$$

An accurate non-BOA (NBO) wave function, determined by a new procedure detailed elsewhere,¹⁹ furnishes a correspondingly accurate (NBO) EFD that serves as a touchstone for judging the quality of $\langle \mathbf{j}_{e,SCC}(\rho,z,t) \rangle$. It is noted that the

standard used here agrees well with the previously employed one,⁴ which, however, provides the EFD only on a rather coarse, nonuniform grid. The main advantage of the new NBO method in the present context is that it can provide the wave function on an arbitrarily fine, uniform grid in the ρ - z plane and hence permits a highly accurate representation of the ρ -component of the EFD in the vicinity of the internuclear axis (on which $\langle j_{\rho} \rangle$ vanishes, according to eq 13).

We summarize the essentials of the new NBO method. The complete Hamiltonian represented in a basis of one-center B-spline functions is first diagonalized to obtain the vibronic energy eigenfunctions $\psi_k(r, \theta, R)$ and eigenvalues E_k , where r and θ are spherical polar coordinates whose origin is the NCM. The absence of φ from the list of arguments of ψ_k is consequent on the cylindrical symmetry. The NBO wave function is then expressed as

$$\Psi_{\text{NBO}}(r, \theta, R, t) = \sum_k c_k \psi_k(r, \theta, R) \exp(-iE_k t / \hbar) \quad (20)$$

The (constant) coefficients, which are determined from a knowledge of the initial wave function, taken to be

$$\Psi_{\text{NBO}}(r, \theta, R, 0) = \psi_0(r, \theta, R - \bar{R}) \quad (21)$$

by analogy with eq 2, are given by

$$c_k = \int_0^\infty dR \int_0^\infty dr r^2 \int_0^{2\pi} d\varphi \times \int_0^\pi d\theta \sin \theta \psi_k(r, \theta, R) \psi_0(r, \theta, R - \bar{R}) \quad (22)$$

For the present case of the nondissociating, nonionizing, oriented H_2^+ the summation on k in eq 20 is restricted to vibronic states whose energies lie below the dissociation threshold. From eq 10b we deduce the following formulas for the components of the NBO flux densities

$$\begin{aligned} \langle j_{e,\text{NBO}}(r, \theta, t) \rangle &= \frac{\hbar}{2i\mu_e} \int_0^{2\pi} d\varphi \int_0^\infty dR \left\{ \Psi_{\text{NBO}}^*(r, \theta, R, t) \right. \\ &\times \left[\sin \theta \frac{\partial}{\partial r} + \frac{\cos \theta}{r} \frac{\partial}{\partial \theta} \right] \Psi_{\text{NBO}}(r, \theta, R, t) - \text{c.c.} \Big\} \mathbf{e}_\rho \\ &+ \frac{\hbar}{2i\mu_e} \int_0^{2\pi} d\varphi \int_0^\infty dR \left\{ \Psi_{\text{NBO}}^*(r, \theta, R, t) \right. \\ &\times \left[\cos \theta \frac{\partial}{\partial r} - \frac{\sin \theta}{r} \frac{\partial}{\partial \theta} \right] \Psi_{\text{NBO}}(r, \theta, R, t) - \text{c.c.} \Big\} \mathbf{e}_z \\ &\equiv \langle j_{\rho,\text{NBO}}(r, \theta, t) \rangle \mathbf{e}_\rho + \langle j_{z,\text{NBO}}(r, \theta, t) \rangle \mathbf{e}_z \end{aligned} \quad (23a)$$

$$\begin{aligned} \langle j_{n,\text{NBO}}(R, t) \rangle &= \frac{\hbar}{2i\mu_n} \int_0^\infty dr r^2 \int_0^\pi d\theta \sin \theta \\ &\times \int_0^{2\pi} d\varphi \left[\Psi_{\text{NBO}}^*(r, \theta, R, t) \frac{\partial}{\partial R} \Psi_{\text{NBO}}(r, \theta, R, t) - \text{c.c.} \right] \end{aligned} \quad (23b)$$

For the numerical evaluations performed as described below, we set the formally infinite upper bounds on the integrations on R indicated in eqs 22 and 23 to $R_{\text{max}} = r_{\text{max}} = 10 a_0$. The nuclear wave packet (probability density) is negligible beyond $R_{\text{max}} \simeq 6 a_0$ and the electronic wave packet is likewise negligible beyond the distance of $10 a_0$ from the NCM for any value of R

less than R_{max} . (The accuracy of the NBO wave function is controlled essentially by three parameters: N_r , N_R , and N_θ , respectively the number of B-splines in the r - and R -dimensions and the number of partial waves included in the basis set.¹⁹ These are chosen so that the vibronic eigenvalues are converged to a precision of $10^{-4} E_h$.)

For the purpose of evaluating partial derivatives and the integral in the expressions given in eqs 16 through 18, we characterize $\langle j_{ez,\text{CC}} \rangle$ and $d_{e,\text{BO}}$ discretely on a grid in the ρ - z plane. The domains of ρ and z are, respectively, $0 \leq \rho \leq 8 a_0$ and $-8 a_0 \leq z \leq 8 a_0$. The grid comprises 100 and 200 equally spaced points in the ρ - and z -dimensions, respectively; the grid size is $0.08 a_0$. The size of the time step is fixed at $0.01523 \hbar/E_h$ (0.368 as). We use the central-difference formula²³ to estimate the partial derivatives. For example, we have

$$\left. \frac{\partial f(\rho, z, t)}{\partial \rho} \right|_{\rho=\rho_i; z=z_j; t=t_k} \simeq \frac{f(\rho_i + \Delta\rho, z_j, t_k) - f(\rho_i - \Delta\rho, z_j, t_k)}{2\Delta\rho} \quad (24)$$

where $\Delta\rho$ is the grid spacing. Integrations are performed by means of the simple trapezoidal rule.²³ The integration on ρ' in eq 18, for instance, is approximated as

$$\begin{aligned} \int_0^\rho d\rho' \rho' F(\rho', z, t) \Big|_{z=z_j; t=t_k} \\ \simeq \sum_i [\rho'_i F(\rho'_i, z_j, t_k) + \rho'_{i+1} F(\rho'_{i+1}, z_j, t_k)] \Delta\rho / 2 \end{aligned} \quad (25)$$

As a test of the viability of the numerical techniques for the estimation of $\langle j_{\rho} \rangle$ by eq 14, we take the NBO electronic probability ($d_{e,\text{NBO}}$) and flux ($\langle j_{ez,\text{NBO}} \rangle$) densities as “input” to the integrand and find the “output” ($\langle j_{\rho,\text{NBO}} \rangle$) to be in precise accord with $\langle j_{\rho,\text{NBO}} \rangle$ computed directly from the expression in eq 23a.

3. RESULTS AND DISCUSSION

Because the calculation of $\langle j_{ez,\text{CC}} \rangle$ has already been detailed,¹⁷ the present focus is on the hierarchical computation of $\langle j_{ez,\text{SCC}} \rangle$ and $\langle j_{\rho,\text{SCC}} \rangle$ according to eqs 16 and 18, respectively. We consider four times that correspond to particular conditions of the bond during the first half-cycle of the large-amplitude vibration: $t = 0.00$ fs, when the bond is initially stretched from its equilibrium length; $t = 3.00$ fs, which marks the onset of the compression of the bond; $t = 6.45$ fs, when the bond length is decreasing at maximum rate (i.e., the nuclear wave packet is running through the minimum of the potential energy curve at maximal rate toward smaller R); $t = 11.05$ fs, when the bond is close to maximum compression (i.e., when the nuclear wave packet is changing direction and beginning to run toward larger R , describing the bond as it begins to lengthen during the second half-cycle of the vibration). Some aspects of the coupled electronic-nuclear dynamics at $t = 6.45$ and 11.05 fs have already been discussed.^{4,17} Here we first systematically compare the CC results, which function as “input” to our hierarchical scheme, with their accurate correlates obtained by the new NBO method.¹⁹ We next compare the scaled CC (SCC) with the NBO EFDs (i.e., the two-dimensional vector fields $\langle j_{e,\text{SCC}} \rangle$ and $\langle j_{e,\text{NBO}} \rangle$).

Figures 1–3 display key quantities that enter the computation of $\langle j_{\rho} \rangle$ via eq 18. (Throughout this section all quantities are expressed in atomic units, unless otherwise indicated.) In general the BOA and NBO results are in quite good agreement. Here we focus on small discrepancies between them. Comparison of the

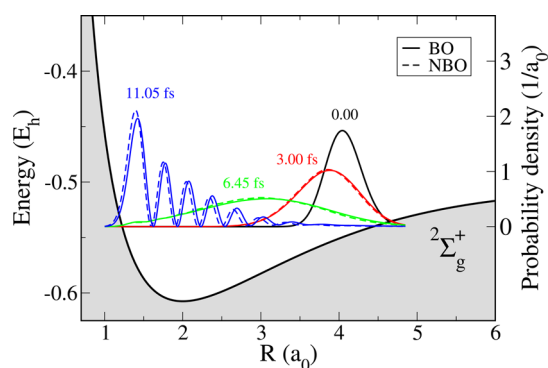


Figure 1. Comparison of Born–Oppenheimer (BO) and non Born–Oppenheimer (NBO) nuclear probability densities superposed on a plot of ground-state potential energy curve at characteristic times $t = 0, 3.00, 6.45, 11.05$ fs. The left ordinate is energy; the right ordinate is probability density.

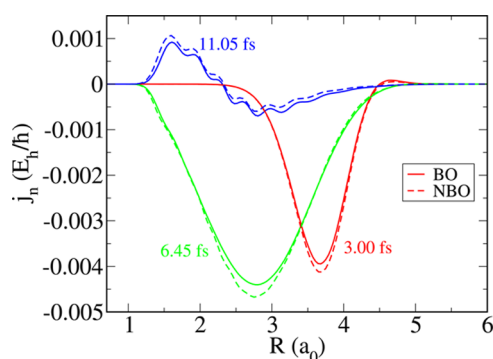


Figure 2. Comparison of BO and NBO nuclear probability flux densities j_n at characteristic times $t = 0, 3.00, 6.45, 11.05$ fs.

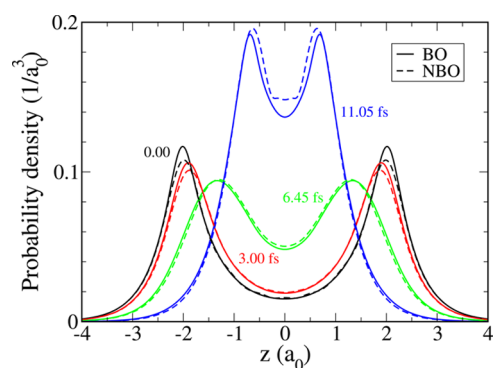


Figure 3. Comparison of BO and NBO electronic probability densities on the internuclear axis ($\rho = 0$) at characteristic times $t = 0, 3.00, 6.45, 11.05$ fs.

BOA and NBO nuclear probability densities, which are shown in Figure 1 superposed on the BOA potential energy curve for the characteristic times $t = 0.00, 3.00, 6.45,$ and 11.05 fs, suggests that the NBO bond length (i.e., the bond length computed from the NBO wave function) decreases with time slightly more rapidly than its BOA counterpart. Already at $t = 3.00$ fs the NBO nuclear wave packet is perceptibly ahead of the BOA packet. Moreover, at $t = 6.45$ fs the NBO packet exhibits a discernible quantum interference pattern engendered by the incipient encounter of the “head” of the packet (i.e., the portion near $R \simeq 1.5 a_0$) with the repulsive region of the potential energy (where the protons come close). The interference pattern is most pronounced at

$t = 11.05$ fs, because of the overlap of the “tail” of the nuclear packet, which is still running toward small R (i.e., bond compression), and the “head”, which has already turned and is running toward larger R (i.e., bond stretch). At this characteristic time the NBO packet is about 130 as ahead of the BOA packet (i.e., the BOA nuclear probability density shown in Figure 1 at $t = 11.05$ fs resembles the NBO nuclear density at 10.92 fs). The more rapid contraction of the NBO bond compared with the BOA bond is evident as well in the plots of the nuclear flux densities in Figure 2. Observe, in particular, that the nuclear flux density at $t = 11.05$ fs consists of positive and negative parts corresponding to the “head” and “tail” of the probability density (Figure 1), which run, respectively, toward larger (bond stretch) and smaller (bond compression) values of R , in accord with the previous discussion¹⁷ of the interference pattern at this characteristic time.

That the NBO wave function runs slightly ahead of the BOA one can be rationalized by the fact that the energies of the BOA vibronic eigenstates lie below those of the corresponding exact ones.²⁴ Moreover, the variational NBO approach, in which the total Hamiltonian is represented in a finite basis, necessarily gives energy eigenvalues that lie above, albeit only slightly, the exact ones. As a consequence, the phases of the NBO wave function increase more rapidly than would those for the hypothetical wave function in which the NBO energies ($\{E_k\}$, eq 20) were replaced by the BOA ones. Hence, the NBO wave function evolves faster than the BOA one.

The slightly faster evolution of the NBO wave function compared with the BOA wave function is also reflected in the corresponding time-dependent *electronic* probability densities plotted in Figure 3. For example, at $t = 6.45$ fs the BOA electron density is lower near the center of the bond ($z = 0$) (and correspondingly higher in the region ($|z| > 1.5 a_0$) outside) than the NBO density, which indicates that the rate of bond formation is lower for the BOA than for the NBO. The difference in rates is even more pronounced at $t = 11.05$ fs. We observe, however, an opposing trend, namely, that for sufficiently large bond distances (e.g., at $t = 0.00$ fs and $t = 3.00$ fs), the BOA electronic probability density is slightly larger than its NBO counterpart in the vicinity of the nuclei. This is a consequence of the fact that the cusp of the electronic wave function at a nucleus is represented better by the BOA wave function (with the present high-level basis set) than by the NBO wave function.

Figure 4 compares the approximate CC z -component of the EFD with its accurate NBO correspondent. Though the CC

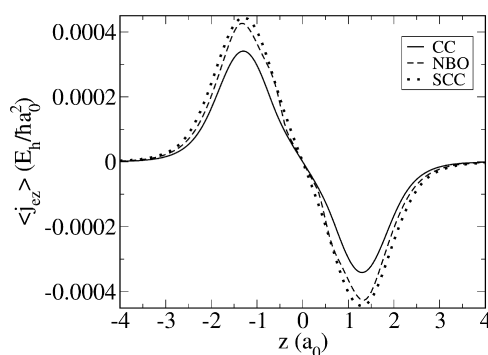


Figure 4. Comparison of CC, SCC, and NBO z -components of electronic flux density $\langle j_{ez} \rangle$ on internuclear axis ($\rho = 0$) at characteristic time $t = 6.45$ fs.

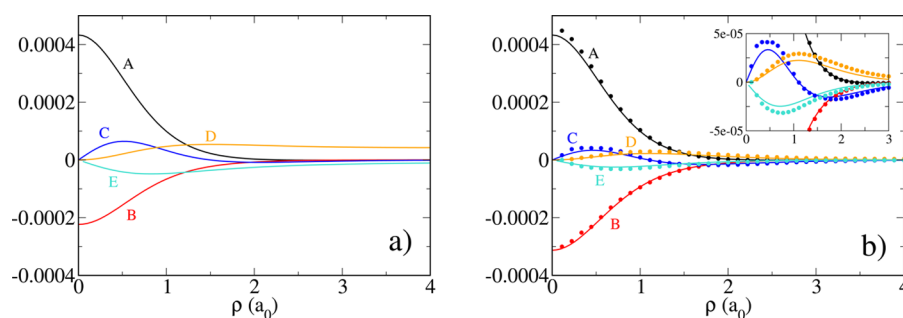


Figure 5. (a) Intermediate quantities involved in computation of radial component of EFD in $z = 0$ plane at characteristic time $t = 6.45$ fs, according to eq 18 with $\lambda(z,t) = 1$: $\partial d_{e,BO}/\partial t$ (A); $\partial \langle j_{ez,SCC} \rangle / \partial z$ (B); $\partial \langle j_{ez,SCC} \rangle / \partial z + \partial d_{e,BO}/\partial t$ (C); $\rho [\partial \langle j_{ez,SCC} \rangle / \partial z + \partial d_{e,BO}/\partial t]$ (D); $\langle j_{ep,SCC}(\rho, z, t) \rangle = \rho^{-1} \int_0^\rho d\rho' \rho' [\lambda(z,t) \partial \langle j_{ez,CC} \rangle / \partial z + \partial d_{e,BO}/\partial t]$ (E). (b) same as (a), except $\lambda(z,t) = 1.4$. Dots refer to NBO quantities. Inset shows blow-up. All quantities are in atomic units.

and NBO curves have similar shapes, the magnitude of $\langle j_{ez,CC} \rangle$ is a bit smaller than that of $\langle j_{ez,NBO} \rangle$. Referring to eq 7, which gives the formula for $\langle j_{ez,CC} \rangle$, we may garner some insight into the source of the error. We observe that the integrand on the right-hand side is the product of an effective electronic probability density ($\Delta_b - \Delta_a$) and the nuclear flux density $^{1/2} j_{n,BO}$. The electronic factor is affected by the delocalization of the component of the electronic wave function $\Phi_{0\alpha}$ associated with one nucleus α (a or b), which penetrates from the domain of that nucleus well into the domain of the other (eq 4b). Therefore, the magnitude of the difference between the a - and b -components tends to be “small” (compared with a hypothetical alternative, more localized, partitioning of the total electronic density (eq 4d)). Moreover, as Figure 2 indicates, the magnitude of the nuclear factor $j_{n,BO}$ also tends to be smaller than that of its accurate correlate $j_{n,NBO}$. The result of these two cooperative trends is that the magnitude of $\langle j_{ez,CC} \rangle$ is uniformly smaller than that of $\langle j_{ez,NBO} \rangle$. The most significant consequence of this discrepancy is that the magnitude of $\partial \langle j_{ez,CC} \rangle / \partial z$ (i.e., the z -component of the gradient of the EFD, which is one of the two quantities appearing in the formula for the ρ -component of the EFD (eq 18)), is smaller than its NBO counterpart.

Let us now demonstrate how the “input” $\langle j_{ez,CC} \rangle$ from the first step of our hierarchical method is used to carry out the second step (i.e., the evaluation of the “output” $\langle j_{ep,CC} \rangle$ according to eq 18). For the particular case $z = 0$ and $t = 6.45$ fs, for example, Figure 5a displays plots of successive intermediate quantities versus ρ that lead from the “inputs” $\partial \langle j_{ez,CC} \rangle / \partial z$ and $\partial d_{e,BO}/\partial t$ to the “output” $\langle j_{ep,CC} \rangle$: $\partial d_{e,BO}/\partial t$ (A); $\partial \langle j_{ez,CC} \rangle / \partial z$ (B); $\rho [\partial \langle j_{ez,CC} \rangle / \partial z + \partial d_{e,BO}/\partial t]$ (C); $\int_0^\rho d\rho' \rho' [\partial \langle j_{ez,CC} \rangle / \partial z + \partial d_{e,BO}/\partial t]$ (D); $\langle j_{ep,CC} \rangle = -\rho^{-1} \int_0^\rho d\rho' \rho' [\partial \langle j_{ez,CC} \rangle / \partial z + \partial d_{e,BO}/\partial t]$ (E). In the following discussion we refer to these quantities simply by their labels. Thus, A and B are the “inputs”; C is the integrand of the expression in eq 18; D is the integral; E is the “output”. We consider first the hypothetical case of no scaling (i.e., $\lambda(z,t) = 1$) corresponding to $\langle j_{ep,CC} \rangle$. We notice at once that the hypothetical “output” E does not satisfy the fourth constraint (eq 15), because the underlying quantity D approaches a nonzero plateau, instead of the correct limiting value. This failure, which can readily be traced to errors in the “input,” is clearly a consequence of the fact that the areas under the positive and negative domains of C do not precisely compensate each other. Indeed, the magnitude of the area under the negative domain of C is too small. This suggests that the shape of the curve B may well be close to that of the accurate NBO correspondent, but its magnitude is smaller than

that of the NBO. This is, of course, apparent in the plots of Figure 4, as discussed above.

The hypothetical “output” shown in Figure 5a is illuminating, though inadequate, because the implicit guess $\lambda(z=0, t=6.45\text{fs}) = 1$ violates the boundary condition in eq 15. As a final step, however, using eq 17 with the CC “inputs”, we obtain a scaling factor of $\lambda(z=0, t=6.45\text{fs}) = 1.4$, which, when inserted into eq 18, yields the new (scaled) CC curves shown in Figure 5b. Of course, A in Figure 5b is the same as A in Figure 5a. By construction, eq 17 forces the areas under the positive and negative domains of C to cancel each other. D therefore approaches the correct asymptotic limit, and, as a consequence, E, which represents the scaled “output” $\langle j_{ep,SCC}(\rho, z=0, t=6.45\text{fs}) \rangle$ satisfies the boundary condition stated in eq 15. Figure 5b also exhibits the analogous curves A–D that lead to the accurate NBO curve E. The agreement of the intermediate (curves A–D) and final (curve E) scaled CC and NBO results is seen to be good. Similar accord is observed for other values of z and t .

Thus, the scaled CC results $\langle j_{ep,SCC}(\rho, z, t) \rangle$ and $\langle j_{ez,SCC}(\rho, z, t) \rangle$ provide the ρ - and z -components of the two-dimensional vector field of the EFD, $\langle \mathbf{j}_{e,SCC}(\rho, z, t) \rangle$. This is represented by arrows and compared with the corresponding NBO EFD, in Figure 6a–c for the selected three characteristic times $t = 3.00$, 6.45 , and 11.05 fs. An enlargement of Figure 6c is shown in Figure 6d. Figure 6e compares the SCC EFD at $t = 11.05$ fs with the NBO EFD at $t = 10.92$ fs. The overall agreement of the SCC EFD with the NBO reference is excellent. On the scale of the plots in Figure 6a–c one can hardly discern any difference between the approximate SCC EFD and its accurate NBO counterpart. In particular, the z -component of the EFD normally dominates the ρ -component, except in the vicinity of the plane $z = 0$, where the z -component vanishes on account of symmetry. But the magnitude of the ρ -component is also quite small there compared with the magnitudes of the z -components at points well away from the $z = 0$ plane.

The blow-up shown in Figure 6d reveals, nevertheless, some significant discrepancies between the SCC and NBO EFDs at $t = 11.05$ fs when bond compression is changing to bond stretching. To explain these deviations, we recall that this switching of directions of the EFD occurs during an interval of only a few hundred attoseconds (i.e., the arrows representing the EFD in Figure 6d change their direction within a few hundred attoseconds). Actually, the switching of directions is marked by two planes, $z = \pm z_s$, on which the EFD vanishes. Apparently these two “switching planes” (corresponding to the front of the switch of direction of the EFD) move from $z_s = 0$

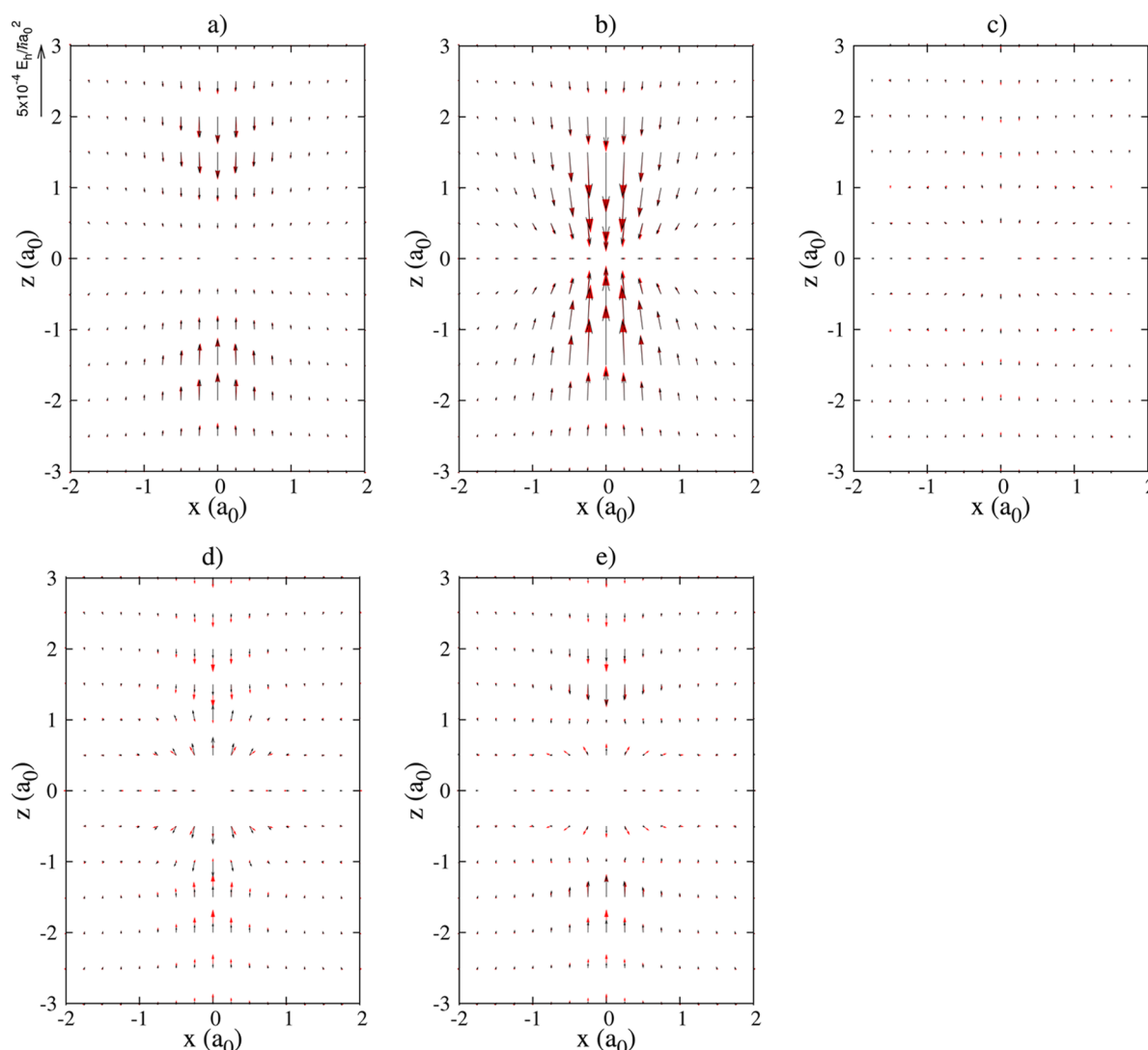


Figure 6. Vector fields comparing SCC (black arrows) and NBO (red arrows) EFDs at characteristic times $t = 3.00$ (a), 6.45 (b), 11.05 (c) fs. The magnitude is indicated by the inset (the distance between tic marks corresponds to $5 \times 10^{-4} E_h / \hbar a_0^2$). Fields shown in (d) are those for $t = 11.05$ fs magnified by a factor of 4; fields shown in (e) correspond to SCC at $t = 11.05$ fs and NBO at $t = 10.92$ fs.

toward increasing values of z . For example, from Figure 6d one can infer that at $t = 11.05$ fs the switching planes for the SCC EFD (red arrows) are close to $z = \pm 1.0 a_0$, whereas the switching planes for the NBO EFD (black arrows) are around $z = \pm 1.3 a_0$. The above analysis shows that this rather small, but non-negligible, discrepancy is due to the slightly faster evolution of the NBO wave packet compared with the BOA one. As indicated above, the NBO packet is roughly 130 as ahead of the BOA packet. Taking this disparity into account, we compare in Figure 6e the NBO EFD at $t = 10.92$ fs with the SCC EFD at $t = 11.05$ fs. These times correspond roughly to the same moment during the switching of directions. We see (Figure 6e) that the switching planes nearly coincide at $z = \pm 1.0 a_0$. As anticipated, the agreement between the time-displaced EFDs (Figure 6e) is markedly better than that between the equal-time EFDs (Figure 6d). Thus, with the recognition of the slightly faster evolution of the NBO wave packet compared with the BOA packet, the agreement between the SCC and reference NBO EFDs must be considered very good, even in the intervals when the EFD is switching directions.

We remark that the pattern of the EFD at times near $t = 11.05$ fs (i.e., at times during the interval when bond compression is turning to bond stretching), which exhibits contiguous regions (separated by the switching planes) in which the flows of the electrons are at once oppositely directed, is a quantum phenomenon quite analogous to that displayed by the nuclear flux density, the plot of which at $t = 11.05$ fs in Figure 3 shows that the sign of $j_{n,BO}$ for $0 < R \leq \sim 2.3 a_0$ is opposite the sign of $j_{n,BO}$ for $R > \sim 2.3 a_0$. In contrast, a classical molecular dynamics simulation of the nuclear motion yields strictly unidirectional nuclear and electronic probability flux densities. The nuclear flux density j_n is proportional to nuclear velocity (i.e., j_n is strictly negative during bond compression and strictly positive during bond stretching).¹⁸ The EFD is parallel with j_n . Hence, everywhere in the ρ - z plane the EFD points normally toward the plane $z = 0$ as the bond shortens (i.e., as the nuclei move toward the classical turning point) or normally away from that plane as the bond lengthens (i.e., as the nuclei retreat from the classical turning point). At no time during the contraction–expansion cycle do regions appear in which the directions of electron flow oppose each other.

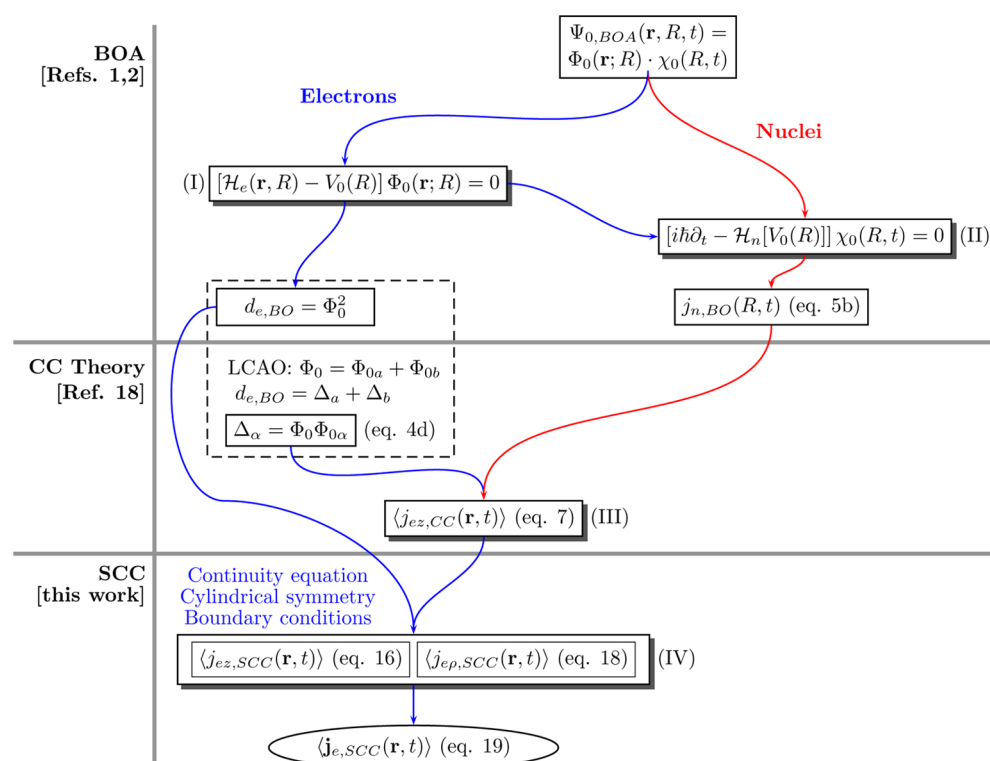


Figure 7. Flowchart depicting the four-level BOA → CC → SCC hierarchy.

4. SUMMARY AND CONCLUSIONS

The present hierarchical approach to the computation of the EFD in oriented H_2^+ vibrating in the electronic ground state $2\Sigma_g^+$ is recapitulated in the flowchart presented in Figure 7. It begins with the traditional BOA, which calls for two standard tasks to be performed sequentially. First, the Born–Oppenheimer electronic energy eigenvalue equation must be solved for the ground-state eigenfunction $\Phi_0(\mathbf{r}; R)$ and eigenvalue $V_0(R)$ as a parametric function of the internuclear distance R . $V_0(R)$ serves as the effective potential energy governing the nuclear motion. Second, the nuclear Schrödinger equation must be solved for the time-dependent nuclear wave packet $\chi_0(R, t)$. From $\Phi_0(\mathbf{r}; R)$ one can calculate the electronic probability density $d_{e,BO}$ and from $\chi_0(R, t)$ the nuclear probability density $d_{n,BO}$ and probability flux density $j_{n,BO}$. The procedures to accomplish these consecutive steps are well established within the framework of traditional quantum chemistry (QC) and quantum dynamics (QD). In the present context we consider levels I and II of the hierarchy (Figure 7) to constitute the tasks of QC and QD, respectively.

Using the LCAO MO method of QC, we can decompose $d_{e,BO}$ into components Δ_a and Δ_b associated with the individual nuclei. These are combined to form an effective electronic probability density associated with the nuclear motion, which is multiplied by $j_{n,BO}$ from QD. The resulting product is then integrated over R to obtain the CC formula for the z -component of the EFD. The construction of $\langle j_{ez,CC} \rangle$ represents level III of the hierarchy. Finally, level IV provides the scaled CC EFD. The scaling enforces four constraints on the SCC EFD (i.e., the satisfaction of the electronic continuity equation, the cylindrical symmetry, and two boundary conditions on the ρ -component), which give rise to the key formula in eq 18 relating the scaled “input” $\langle j_{ez,SCC}(\rho, z, t) \rangle$ to the scaled “output” $\langle j_{e\rho,SCC}(\rho, z, t) \rangle$ (Figure 7).

The excellent agreement of the approximate SCC EFD with the accurate NBO reference EFD, which is documented in Figure 6, implies that the hierarchical approach accounts properly for the physics. As described in the BOA, the process that gives rise to the nonzero EFD, namely vibration in the present case of the oriented H_2^+ , is electronically adiabatic. Calculation of the EFD requires a knowledge of only the ground-state wave function; nonadiabatic couplings to electronic excited states are immaterial. (In marked contrast, several previous approaches utilize these couplings to achieve a nonvanishing EFD; see section 1.) The BOA → CC → SCC hierarchy thus reflects the simple, intuitive BO picture: the spatial distribution of the light, fast electrons adjusts instantly in response to the motion of the heavy, slow nuclei. The EFD is produced by the relative motion of the instantaneously evolving electron clouds localized on the individual nuclei. Observe, however, that the EFD itself evolves on the relatively long time scale of the nuclear motion (i.e., of the order of tens of femtoseconds for the particular state of H_2^+ under consideration). It is remarkable that this simple BO picture was obscured from the beginning by the paradoxical result $\langle j_{e,BOA}(\mathbf{r}, t) \rangle = \mathbf{0}$.³ The present hierarchical procedure provides a resolution of this well-known, long-standing enigma.

We hope that this work stimulates applications of the hierarchy to more demanding processes and systems. Examples that come readily to mind include laser-driven dissociation of H_2^{+25} as well as vibrating or dissociating heteronuclear diatomics such as HD^+ and multielectron linear molecules such as H_2 , HeH^+ , Li_2 , and HCCH . Further, because the CC theory has recently been generalized to encompass nonlinear polyatomic systems,²⁶ the extension of the hierarchical approach to such systems merits investigation. Additional purely theoretical studies also suggest themselves. For instance, one may seek a basis for an invariant apportionment of the electron probability density

between the individual nuclei ($d_{\text{e,BO}} = \Delta'_a + \Delta'_b$) different from the present one, which is based on LCAO MO representation of Φ_0 .

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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