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Electron Transition Current Density in Molecules. 1. Non-Born−Oppenheimer Theory of Vibronic and Vibrational Transitions

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The one-particle electron transition current density (TCD) for vibronic transitions between pairs of stationary states in molecules is defined. Expressions for TCD are developed using the complete adiabatic (CA) formalism in which the electronic wave function carries an explicit dependence on the nuclear momenta, as well as the usual dependence on nuclear positions. In the case of vibronic transitions, the principal non-Born−Oppenheimer (non-BO), nuclear-momentum-dependent contribution to TCD is accompanied by a less important BO, nuclear-position-dependent contribution. For vibrational transitions within a single electronic state, the BO contribution vanishes, leaving only non-BO, nuclear-momentum-driven TCD. In the limit of pure electronic transitions, or vibrational transitions within a single electronic state, it is shown that electron TCD satisfies the continuity equation for the conservation of electron transition probability density (TPD) for any pair of stationary states. TCD is a vector field having a unique representation at each point in the Cartesian space of a molecule. It is shown that TCD is a dynamic representation of the changes in TPD associated with electrons in molecules under the influence of a transition-inducing perturbation and that it provides direct visual information concerning the participation of all spatial regions of the molecule in quantum transitions. The use of TCD provides an opportunity to view uniquely electronic motion associated with quantum mechanical transitions in molecules.

Introduction

By far, the most common visual representation of electrons in molecules is the electron probability density, the absolute square of the electronic wave function.[1,2] For electronic transitions, it is possible to represent the *changes* in electron density in terms of electron probability difference maps, and similarly, for vibrational transitions, it is possible, but not common, to represent changes in electron probability density with nuclear motion in terms of difference maps.[3] Although these density difference maps provide some useful information with regard to changes in probability density during transitions, they are only scalar fields.

A second, fundamental density function that can be defined for every electron wave function is the electron probability current density.[4,5] The current density is a vector field, the magnitude and direction of which are defined at every point in the space of the wave function. Electron current density describes the spatial flow of electron probability that is a result of changes in the latter with time. Since electron probability cannot be lost or gained in a closed system, such as a stable molecule, the electron probability density is a conserved quantity and obeys the continuity equation relating the electron probability and current density functions,

$$-\nabla\cdot\mathbf{j} = \frac{\partial\rho}{\partial t} \tag{1}$$

Here, at every point in the space of the molecule, the negative spatial gradient of the current density equals the rate of change with time of the electron probability density. This is a fundamental relationship between these two electron-density functions.

For molecules in stationary states, there is no change in the probability density with time, and hence, from eq 1, the electron current density must vanish at all points in space. Since most applications of quantum mechanics to molecular systems involve considerations of stationary states, there has been little motivation to consider electron current density as a means to visualize electronic motion within individual quantum states in molecules.

Recently,[6] we demonstrated that electron current density can be defined for *pairs* of simple electronic orbitals in atomic and molecular systems. In this case, two stationary states can exhibit electron *transition* current density (TCD) associated with the oscillations of electron probability density that occur under the influence of perturbations that induce electronic transitions between these two states. In this context, electron current density emerges as a valuable visual tool from which to learn more about electronic motion associated with *transitions* between pairs of stationary states.

In this paper, we extend the formalism of electron TCD to include explicitly multielectron wave functions, vibronic detail in electronic transitions, and, as a special case, pure vibrational transitions within a single electronic state. To achieve these objectives, we employ complete adiabatic (CA) wave functions, defined and developed previously.[7,8] These wave functions are factored products of electronic and vibrational wave functions in the Born−Oppenheimer (BO) sense but include the lowest-order non-BO contribution through an explicit dependence of the electronic part of the wave function on the nuclear momenta (or velocities) as parametric (classical) variables. The nonfactorable nature of the non-BO part of the wave function can be recovered, whenever desired, by converting the classical nuclear momenta to their quantum mechanical form and allowing them to operate on the nuclear, vibrational part of the wave function.

Including non-BO contributions is indispensable to the description of electron current density induced by molecules undergoing vibrational transitions, and the CA formalism provides a particularly appealing way to understand the interplay between the oscillation of electron probability and current

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densities during vibrational motions. In particular, changes in probability density can be correlated to nuclear positions (displacements) and are described within the BO approximation in accordance with the right-hand side of eq 1, whereas current density is induced by and correlated with nuclear velocities using pure non-BO contributions. The right- and left-hand sides of eq 1 are then governed by BO and non-BO contributions, respectively, and yet equal one another exactly, thereby achieving conservation of electron transition probability density. As shown in section III, the case of vibronic transitions is more complex and it is found that both BO and non-BO contributions occur for the electron probability density (TPD) and TCD, albeit to different degrees.

Theoretical Background

As background for the development of expressions for vibronic and vibrational TCD, we provide general definitions for the electron TCD and TPD functions and demonstrate that these transition densities obey the continuity equation. In addition, we present the direct relationship between TCD and the velocity form of the electric-dipole transition moment, the absolute square of which is proportional to the electric-dipole absorption intensity of the transition.

1. Definition of Transition Current Density. We define the multiparticle time-dependent molecular wave function associated with a nondegenerate stationary state n as

$$\tilde{\Psi}_n(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, \mathbf{R}, t) = \Psi_n(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, \mathbf{R}) \exp(-i\omega_n t) \tag{2}$$

where the electron positions $\mathbf{r}_i$ are enumerated explicitly, while the nuclear positions are simply represented by $\mathbf{R}$. The tilde over the wave function symbol denotes a complex quantity, which, in the case of a nondegenerate stationary state, arises solely from its time dependence, as indicated in eq 2. The radial frequency is given by $\omega_n = E_n/\hbar$, where E_n is the energy of state n and $\hbar$ is Planck's constant divided by 2π. The single-particle electron probability density for state n is given by

$$\rho_n(\mathbf{r}_1, t) = \int \tilde{\Psi}_n^*(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, \mathbf{R}, t) \times \tilde{\Psi}_n(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, \mathbf{R}, t)\, d\mathbf{r}_2, ..., d\mathbf{r}_N, d\mathbf{R} \tag{3}$$

where we integrate the absolute square of the wave function over all particle coordinates except those of electron 1. Since only one electronic position remains, and since all electrons are indistinguishable, we can write the electron probability density more simply as

$$\rho_n(\mathbf{r}, t) = \tilde{\Psi}_n^*(\mathbf{r}, t)\tilde{\Psi}_n(\mathbf{r}, t) = \Psi_n^{\,2}(\mathbf{r}) = \rho_n(\mathbf{r}) \tag{4}$$

where we have suppressed the reference to coordinates over which we have integrated in eq 3. In the second part of this equation, we show that the electron probability density for a nondegenerate stationary state is time independent, since the product of the exponential time-dependent factor, given in eq 2, multiplied by its complex conjugate is unity.

The single-electron current density for state n is defined as

$$\mathbf{j}_n(\mathbf{r}_1, t) = \frac{\hbar}{2mi}\int [\tilde{\Psi}_n^*(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, \mathbf{R}, t)(\nabla_1 + ... + \nabla_N) \times \tilde{\Psi}_n(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, \mathbf{R}, t) - \tilde{\Psi}_n(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, \mathbf{R}, t)(\nabla_1 + ... \nabla_N) \times \tilde{\Psi}_n^*(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, \mathbf{R}, t)]\, d\mathbf{r}_2, ..., d\mathbf{r}_N, d\mathbf{R} \tag{5}$$

where $(\nabla_1 + ... + \nabla_N)$ is the vector gradient operator of the electrons. As in eq 4, the time dependence vanishes, and after integrating over all but the coordinates of electron 1, we have

$$\mathbf{j}_n(\mathbf{r}, t) = \frac{\hbar}{2mi}[\Psi_n^*(\mathbf{r})\nabla\Psi_n(\mathbf{r}) - \Psi_n(\mathbf{r})\nabla\Psi_n^*(\mathbf{r})] \tag{6}$$

Since the time-independent wave function, $\Psi_n(\mathbf{r})$, is real, eq 6 vanishes at all points in space. Given the vanishing of the current density and the time independence of eqs 4 and 6, it is clear that the continuity equation given in eq 1 is satisfied. In other words, for a stationary state, the probability density does not change with time and there are no currents.

The situation changes entirely for a nonstationary state. The simplest nonstationary state is a linear combination of two stationary states of different energy where we assume, for simplicity, that the mixing coefficients, c_i, are time independent. This is the case for a small perturbation, which may be periodic, but does not change its strength with time. We label such a state with two subscripts to denote the stationary states n and m as

$$\tilde{\Psi}_{nm}(\mathbf{r}, t) = c_n\tilde{\Psi}_n(\mathbf{r}, t) + c_m\tilde{\Psi}_m(\mathbf{r}, t) \tag{7}$$

and we have, for economy, suppressed the coordinates of the other electrons and the nuclei. The nonstationary-state electron probability density is given by the absolute square of eq 7 and leads to the following expressions:

$$\begin{aligned}\rho_{nm}(\mathbf{r}, t) &= \tilde{\Psi}_{nm}^*(\mathbf{r}, t)\tilde{\Psi}_{nm}(\mathbf{r}, t)\\ &= c_n^{\,2}\rho_n(\mathbf{r}) + c_m^{\,2}\rho_m(\mathbf{r}) + 2c_nc_mO_{nm}(\mathbf{r})\cos \omega_{nm}t\end{aligned} \tag{8}$$

Here, $\omega_{nm} = \omega_n - \omega_m$ is the frequency difference, or beat frequency, between the two stationary states, and the real, time-independent electron transition probability density (TPD) is defined as[6,9]

$$O_{nm}(\mathbf{r}) \equiv \Psi_n(\mathbf{r})\Psi_m(\mathbf{r}) \tag{9}$$

Equation 8 consists of a constant part from the single-state densities and a sinusoidally varying part that depends on the TPD. Both eqs 8 and 9 are symmetric with respect to interchange of indices for states n and m, and no bias toward either state is indicated. However, in the case of a weak perturbation of state n by state m, the single-state term with c_m^2 in eq 8 may dropped as small.

The electron current density for the nonstationary-state nm is given by

$$\begin{aligned}\mathbf{j}_{nm}(\mathbf{r}, t) &= \frac{\hbar}{2mi}[\tilde{\Psi}_{nm}^*(\mathbf{r}, t)\nabla\tilde{\Psi}_{nm}(\mathbf{r}, t) - \tilde{\Psi}_{nm}(\mathbf{r}, t)\nabla\tilde{\Psi}_{nm}^*(\mathbf{r}, t)]\\ &= 2c_nc_m\mathbf{J}_{nm}(\mathbf{r}) \sin \omega_{nm}t\end{aligned} \tag{10}$$

where we have defined the real, time-independent electron transition current density (TCD) as[6]

$$\mathbf{J}_{nm}(\mathbf{r}) \equiv \frac{\hbar}{2m}[\Psi_n(\mathbf{r})\nabla\Psi_m(\mathbf{r}) - \Psi_m(\mathbf{r})\nabla\Psi_n(\mathbf{r})\nabla\Psi_n(\mathbf{r})] \tag{11}$$

Although, overall, eq 10 is symmetric with respect to interchange of subscripts n and m, both the TCD and the sinusoidal time-dependent factor are odd with respect to this interchange. For reasons demonstrated above, the current density also has no single-state time-independent terms and consists only of the time-varying transition cross term that depends equally, but oppositely, on both contributing stationary states. The TCD represents the magnitude and direction of the oscillating vector field of currents that is set in motion when state n is perturbed or mixes with state m, or *vice versa*.

2. Conservation of Transition Probability and Current Density. Because the probability and current densities for the nonstationary state wave function, $\tilde{\Psi}_{nm}(\mathbf{r}, t)$, as given in eqs 8 and 10, are defined in accordance with standard quantum mechanical definitions, eq 1 for this wave function is obeyed. Hence, we can write the continuity equation for the conservation of probability and current density as

$$-\nabla\cdot\mathbf{j}_{nm}(\mathbf{r}, t) = \frac{\partial\rho_{nm}(\mathbf{r}, t)}{\partial t} \tag{12}$$

Using the expressions in eqs 8 and 10 we have that

$$-\nabla\cdot\mathbf{j}_{nm}(\mathbf{r}, t) = -2c_nc_m\nabla\cdot\mathbf{J}_{nm}(\mathbf{r}) \sin \omega_{nm}t \tag{13}$$

$$\frac{\partial\rho_{nm}(\mathbf{r}, t)}{\partial t} = -2c_nc_m\omega_{nm}O_{nm}(\mathbf{r})\sin \omega_{nm}t \tag{14}$$

From eqs 12−14, we can extract the continuity relation for the transition densities TPD and TCD defined above, namely,

$$-\nabla\cdot\mathbf{J}_{nm}(\mathbf{r}) = \omega_{mn}O_{nm}(\mathbf{r}) \tag{15}$$

where we have chosen to reverse the order of the subscripts of the beat frequency with the view that the m state is a higher-energy perturbing state and ω_{mn} will represent a positive frequency difference.

Equation 15 can be verified explicitly by developing further the gradient of the TCD. Recalling that reference to the other electron coordinates, over which integration is performed, has been suppressed for simplicity, we can first write

$$-\nabla\cdot\mathbf{J}_{nm}(\mathbf{r}) = -\int(\nabla_1 + ... + \nabla_N)\cdot\mathbf{J}_{nm}(\mathbf{r}_1, ..., \mathbf{r}_N)\, \mathrm{d}\mathbf{r}_2, ..., \mathrm{d}\mathbf{r}_N \tag{16}$$

Carrying out the gradient operation within the integrand using the generalization of the expression for the TCD in eq 10 to N electrons yields contributions for each electron of the form

$$-\nabla_i\cdot\mathbf{J}_{nm}(\mathbf{r}_i) = -\frac{\hbar}{2m}[\Psi_n(\mathbf{r}_i)\nabla_i^{\,2}\Psi_m(\mathbf{r}_i) - \Psi_m(\mathbf{r}_i)\nabla_i^{\,2}\Psi_n(\mathbf{r}_i)] \tag{17}$$

where the two terms in which the gradient operates separately on each wave function in the product cancel; this leaves only the two quadratic terms. The Laplacian operators in eq 17 can be converted to kinetic energy operators for each of the electrons and from there to the complete Hamiltonian by adding appropriate potential energy terms to the kinetic energy operators. The potential energy terms can, of course, be removed by cancellation of the two terms in eq 17 if desired, since the potential energy operators commute with the wave functions. Summing the contributions of the N electrons in eq 17, we have for eq 16

$$\begin{aligned}-\nabla\cdot\mathbf{J}_{nm}(\mathbf{r}) &= -\frac{\hbar}{2m}\int[\Psi_n(\mathbf{r}_1, ..., \mathbf{r}_N)(\nabla_1^2 + ... + \nabla_N^2) \times \\ &\quad \Psi_m(\mathbf{r}_1, ..., \mathbf{r}_N) - \Psi_m(\mathbf{r}_1, ..., \mathbf{r}_N)(\nabla_1^2 + ... + \nabla_N^2) \times \\ &\quad \Psi_n(\mathbf{r}_1, ..., \mathbf{r}_N)]\, \mathrm{d}\mathbf{r}_2, ..., \mathrm{d}\mathbf{r}_N \\ &= \frac{1}{\hbar}\int[\Psi_n(\mathbf{r}_1, ..., \mathbf{r}_N)H\Psi_m(\mathbf{r}_1, ..., \mathbf{r}_N) - \\ &\quad \Psi_m(\mathbf{r}_1, ..., \mathbf{r}_N)H\Psi_n(\mathbf{r}_1, ..., \mathbf{r}_N)]\, \mathrm{d}\mathbf{r}_2, ..., \mathrm{d}\mathbf{r}_N\end{aligned} \tag{18}$$

The Hamiltonian operator of the molecule yields the energy of the stationary state, E_i, when acting on the corresponding wave function. After suppressing again the dependence on the other electron coordinates, we can write

$$-\nabla\cdot\mathbf{J}_{nm}(\mathbf{r}) = \frac{1}{\hbar}(E_m - E_n)\Psi_n(\mathbf{r})\Psi_m(\mathbf{r}) = \omega_{mn}O_{nm}(\mathbf{r}) \tag{19}$$

which verifies eq 15. We conclude that the TCD and TPD represent, respectively, the electron transition current and probability densities that oscillate at the beat frequency of two coupled stationary states between which quantum mechanical transitions can take place. Any perturbation, such as an electromagnetic field, that is in resonance with the beat frequency can induce transitions between the two states.

3. Relation to the Electric-Dipole Transition Moment. We next consider additional properties of electron TCD. In particular, we define its relationship to electric-dipole transition moments and hence to the absorption (or emission) intensity of electronic transitions in molecules. We consider first the expression for the electronic contribution to the position form of the electric-dipole transition moment

$$(\boldsymbol{\mu}_r)_{mn} = -\int\Psi_m(\mathbf{r})e\mathbf{r}\Psi_n(\mathbf{r})\, \mathrm{d}\mathbf{r} = -e\int\mathbf{M}_{mn}(\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{20}$$

where the transition dipole density (TDD) is defined as

$$\mathbf{M}_{mn}(\mathbf{r}) \equiv \Psi_m(\mathbf{r})\mathbf{r}\Psi_n(\mathbf{r}) = \mathbf{r}O_{mn}(\mathbf{r}) \tag{21}$$

Alternatively, we can write the expression for the contribution of the electrons to the velocity form of the electric dipole transition moment as

$$(\boldsymbol{\mu}_\mathrm{v})_{mn} = -\int\Psi_m(\mathbf{r})e\dot{\mathbf{r}}\Psi_n(\mathbf{r})\, \mathrm{d}\mathbf{r} = -\int\Psi_m(\mathbf{r})\left(\frac{-\mathrm{i}e\hbar}{m}\nabla\right)\Psi_n(\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{22}$$

where a dot over a symbol refers to its classical time derivative. The integrals in eq 22 are odd with respect to interchange of the indices n and m, and hence, we can write the velocity form of the electric-dipole transition moment in terms of the TCD as

$$(\boldsymbol{\mu}_\mathrm{v})_{mn} = \frac{\mathrm{i}e\hbar}{2m}\int[\Psi_m(\mathbf{r})\nabla\Psi_n(\mathbf{r}) - \Psi_n(\mathbf{r})\nabla\Psi_m(\mathbf{r})]\, \mathrm{d}\mathbf{r} = -\mathrm{i}e\int\mathbf{J}_{nm}(\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{23}$$

Comparing eqs 20 and 23, we see that the electric-dipole transition moment can be expressed in terms of either the TDD or the TCD, both of which are vector field densities. In the limit of an exact wave function, the position-dipole and velocity-dipole forms of the electric-dipole transition moment equal one another; however, there is a significant difference between the information carried by the TDD compared to that of the TCD. From eq 21 it can be seen that the vector field represented by $\mathbf{M}_{mn}(\mathbf{r})$ depends critically on the choice of the origin of the coordinate system to which $\mathbf{r}$ is referred. In particular, all the vectors in this field are pointing radially away from the origin of coordinates, and spatial locations in the immediate vicinity of the origin have greatly diminished contributions (moments), and the point at the origin obviously has no contribution. As result, even though the dipole transition moment itself is not origin dependent, its integrand is origin dependent.

On the other hand, $\mathbf{J}_{mn}(\mathbf{r})$ is not origin dependent. This vector field depicts the velocity vector of the probability density at individual points in space as a unique, origin-independent representation. The general preference for the position form over the velocity form of the interaction of radiation with atoms and molecules may be another reason for the absence of use of electron TCD, up to this point, as a visual aid to a more graphic understanding of electronic transitions.

Finally, we note that TCD is a special representation of the integrand of the velocity form of the electric-dipole transition moment, one that obeys the continuity relation in eq 19. In general, the integrand of the velocity form of the electric-dipole moment is not the same as TCD; i.e., TCD requires two terms.

Transition Current Density in Vibronic Transitions

In this section, we extend the theory presented above to the case of vibronic transitions where both electronic and vibrational quantum numbers change during a transition. We use the formalism of the complete adiabatic (CA) approximation, as discussed above, to describe the vibronic wave function.[7,8] In this way the vibronic wave function can be augmented by the lowest order correction to the BO approximation using a notation that puts the nuclear-position and nuclear-velocity dependence of the electronic wave function on an equal footing. Use of the CA approximation also provides a convenient basis for extending the formalism of TCD to pure vibrational transitions.

1. Complete Adiabatic Wave Function. The formalism associated with the CA wave function has been described previously.[7,8] In this section, we summarize the derivation of this wave function to provide a link between the CA approximation and a more rigorous treatment of vibronic transitions. In the CA approximation, the energy of the vibrational substructure of electronic states is ignored relative to the energy spacing between pure electronic states. The approximation is particularly favorable for the description of the nuclear-velocity dependence of the ground electronic state and for excited electronic states well separated from all neighboring electronic states.

We begin by writing, through first-order perturbation by the nuclear kinetic energy operator, the non-BO wave function for a vibronic state ev,

$$\Psi_{\mathrm{ev}}(\mathbf{r},\mathbf{R},) = \psi_{\mathrm{e}}(\mathbf{r},\mathbf{R})\phi_{\mathrm{ev}}(\mathbf{R}) - \sum_{\mathrm{su}\neq\mathrm{ev}} \frac{\langle\psi_{\mathrm{s}}\phi_{\mathrm{su}}|T_N|\psi_{\mathrm{e}}\phi_{\mathrm{ev}}\rangle}{E_{\mathrm{su}}-E_{\mathrm{ev}}}\psi_{\mathrm{s}}(\mathbf{r},\mathbf{R})\phi_{\mathrm{su}}(\mathbf{R}) \quad (24)$$

where the first term is the usual BO product of the electronic and nuclear wave functions and the second term is a perturbation summation over the BO excited vibronic states su. The nuclear kinetic energy operator is given by the sum over all nuclei as

$$T_N = -\hbar^2\sum_A \frac{1}{2M_A}\nabla_A{}^2 \quad (25)$$

In the present context, the most important contribution to the perturbation matrix element is the cross term that couples the electronic and nuclear motions, and this is given by

$$\langle\psi_{\mathrm{s}}\phi_{\mathrm{su}}|T_N|\psi_{\mathrm{e}}\phi_{\mathrm{ev}}\rangle \cong -\hbar^2\sum_{A,\alpha}\frac{1}{M_A}\left\langle\psi_{\mathrm{s}}\left|\frac{\partial}{\partial R_{A\alpha}}\right|\psi_{\mathrm{e}}\right\rangle\left\langle\phi_{\mathrm{su}}\left|\frac{\partial}{\partial R_{A\alpha}}\right|\phi_{\mathrm{ev}}\right\rangle \quad (26)$$

where α refers to a summation over the Cartesian vector components *x*, *y*, and *z*. The nuclear position dependence of the BO electronic wave function can be written as a sum over states as

$$\psi_{\mathrm{e}}(\mathbf{r},\mathbf{R}) = \psi_{\mathrm{e}}^0(\mathbf{r}) + \sum_{\mathrm{s}\neq\mathrm{e},A,\alpha}\langle\psi_{\mathrm{S}}^0|(\partial\psi_{\mathrm{e}}/\partial R_{A\alpha})_0\rangle\psi_{\mathrm{S}}^0(\mathbf{r})R_{A\alpha} \quad (27)$$

where the superscript or superscript zero refers to evaluation of the electronic wave function at the equilibrium nuclear position. This permits us to write the non-BO vibronic wave function to first order in the nuclear coordinates as

$$\tilde{\Psi}_{\mathrm{ev}}(\mathbf{r},\mathbf{R}) = \psi_{\mathrm{e}}^0\phi_{\mathrm{ev}} + \sum_{A,\alpha}\sum_{\mathrm{s}\neq\mathrm{e}}D_{\mathrm{es},A\alpha}^0\psi_{\mathrm{S}}^0R_{A\alpha}\phi_{\mathrm{ev}} + \sum_{A,\alpha}\sum_{\mathrm{su}\neq\mathrm{ev}}\frac{D_{\mathrm{es},A\alpha}^0\psi_{\mathrm{S}}^0\phi_{\mathrm{su}}}{\omega_{\mathrm{su,ev}}}\langle\phi_{\mathrm{su}}|\mathrm{i}\dot{R}_{A\alpha}|\phi_{\mathrm{ev}}\rangle \quad (28)$$

where the symbols used are

$$D_{\mathrm{se},A\alpha}^0 = \langle\psi_{\mathrm{S}}^0|(\partial\psi_{\mathrm{e}}/\partial R_{A\alpha})_0\rangle \quad (29)$$

$$\omega_{\mathrm{su,ev}} = (E_{\mathrm{su}} - E_{\mathrm{ev}})/\hbar \quad (30)$$

and the nuclear velocity operator is given by

$$\dot{R}_{A\alpha} = \frac{-\mathrm{i}\hbar}{M_A}\frac{\partial}{\partial R_{A\alpha}} \quad (31)$$

We now assume that the vibrational detail can be dropped from the frequency denominator in eq 28 by writing $\omega_{\mathrm{su,ev}} \cong \omega_{\mathrm{se}}^0 = (E_{\mathrm{e}}^0 - E_{\mathrm{s}}^0)/\hbar$. This allows summation over all vibrational levels *u* to closure, which eliminates all dependence on the excited-state vibrational wave functions ϕ_{su}. This in turn removes the nuclear velocity operator from the matrix element over the nuclear coordinates and allows the nuclear velocity to become a parametric variable of the electronic wave function. With these approximations, the complete non-BO vibronic wave function is now factorable into a product of a vibrational wave function and an electronic wave function that depends on both nuclear velocity and position. Carrying out these steps leads to the CA vibronic wave function

$$\tilde{\Psi}_{\mathrm{ev}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}}) = \tilde{\psi}_{\mathrm{e}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}})\phi_{\mathrm{ev}}(\mathbf{R}) = \left[\psi_{\mathrm{e}}^0 + \sum_{A,\alpha}\sum_{\mathrm{s}\neq\mathrm{e}}D_{\mathrm{es}}^0\psi_{\mathrm{s}}^0\left(R_{A\alpha} + \frac{\mathrm{i}\dot{R}_{A\alpha}}{\omega_{\mathrm{es}}^0}\right)\right]\phi_{\mathrm{ev}} \quad (32)$$

The nuclear velocity, $\dot{\mathbf{R}}$, is used as a classical variable to specify the velocities of individual nuclei in much the same way that nuclear positions are specified in the determination of the electronic part of the wave function in the BO approximation. Since the CA wave function remains factored into electronic and nuclear parts, it is as an adiabatic wave function, even though the lowest-order non-BO contribution is included. The nonadiabatic nature of this wave function can be restored by replacing the values of the nuclear velocities by their quantum mechanical operators, which then operate on the nuclear (vibrational) wave functions. The use of nuclear velocity derivatives has also been used in a closely related, alternative development of the theory of vibrational circular dichroism by Buckingham and co-workers.[10,11]

The first two terms in square brackets in eq 32 represent the zeroth- and first-order BO expressions for the electronic wave function. The last term is the CA, non-BO term that depends classically on the nuclear velocities. This term is imaginary and leads to a complex electronic wave function in the same way that the perturbation of a molecule with a magnetic field creates electron currents described by a complex wave function. If the nuclear velocities are replaced by their quantum mechanical operators, the molecular wave function becomes real again but is no longer adiabatic in the sense that it is not factorable into electronic and nuclear parts.

2. Complete Adiabatic Vibronic TCD and TPD Expressions. For a transition between states ev and e′v′, we consider the nonstationary-state wave function

$$\tilde{\Psi}_{\mathrm{ev,e'v'}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}},t) = c_{\mathrm{ev}}\tilde{\Psi}_{\mathrm{ev}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}})\exp(-\mathrm{i}\omega_{\mathrm{ev}}t) + c_{\mathrm{e'v'}}\tilde{\Psi}_{\mathrm{e'v'}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}})\exp(-\mathrm{i}\omega_{\mathrm{e'v'}}t) \quad (33)$$

which is a linear combination of the two participating stationary states and whose mixing coefficients are time-independent, or changing very slowly on the time scale of the transition frequencies. The expression for the single-electron time-dependent current density is obtained by substitution of eq 33 into eq 10:

$$\mathbf{j}_{\mathrm{ev,e'v'}}(\mathbf{r},t) = \frac{\hbar}{2mi}\int[\tilde{\Psi}^{*}_{\mathrm{ev,e'v'}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}},t)\nabla\tilde{\Psi}_{\mathrm{ev,e'v'}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}},t) - \tilde{\Psi}_{\mathrm{ev,e'v'}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}},t)\nabla\tilde{\Psi}^{*}_{\mathrm{ev,e'v'}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}},t)]\,\mathrm{d}\mathbf{R} \quad (34)$$

where we integrate over the nuclear coordinates to obtain a single-particle electron current density having no explicit nuclear-position or nuclear-velocity dependence. Using eq 32 for the CA vibronic wave function in eq 33 and keeping terms through first order in the nuclear positions and velocities, we obtain

$$\mathbf{j}_{\mathrm{ev,e'v'}}(\mathbf{r},t) = 2c_{\mathrm{ev}}c_{\mathrm{e'v'}}\mathbf{J}_{\mathrm{ev,e'v'}}(\mathbf{r})\sin\omega_{\mathrm{ev,e'v'}}t \quad (35)$$

where the expression for the time-independent TCD, also defined above in eqs 10 and 11, is given by

$$\mathbf{J}_{\mathrm{ev,e'v'}}(\mathbf{r}) = \Bigg\{\mathbf{J}^{0}_{\mathrm{ee'}}(\mathbf{r})\langle\phi_{\mathrm{ev}}|\phi_{\mathrm{e'v'}}\rangle + \sum_{A,\alpha}[\sum_{\mathrm{s}\neq\mathrm{e'}}D^{0}_{\mathrm{se'},A\alpha}\mathbf{J}^{0}_{\mathrm{es}}(\mathbf{r}) - \sum_{\mathrm{s}\neq\mathrm{e}}D^{0}_{\mathrm{se},A\alpha}\mathbf{J}^{0}_{\mathrm{es}}(\mathbf{r})]\langle\phi_{\mathrm{ev}}|R_{A\alpha}|\phi_{\mathrm{e'v'}}\rangle + \sum_{A,\alpha}\left[\sum_{\mathrm{s}\neq\mathrm{e'}}\frac{D^{0}_{\mathrm{se'},A\alpha}\mathbf{J}^{0}_{\mathrm{es}}(\mathbf{r})}{\omega^{0}_{\mathrm{se'}}} + \sum_{\mathrm{s}\neq\mathrm{e}}\frac{D^{0}_{\mathrm{se},A\alpha}\mathbf{J}^{0}_{\mathrm{e's}}(\mathbf{r})}{\omega^{0}_{\mathrm{se}}}\right]\langle\phi_{\mathrm{ev}}|\mathrm{i}\dot{R}_{A\alpha}|\phi_{\mathrm{e'v'}}\rangle\Bigg\} \quad (36)$$

and where the pure electronic TCD is given in accordance with the general definition in eq 11 as

$$\mathbf{J}^{0}_{\mathrm{ee'}}(\mathbf{r}) = \frac{\hbar}{2m}[\psi^{0}_{\mathrm{e}}(\mathbf{r})\nabla\psi^{0}_{\mathrm{e'}}(\mathbf{r}) - \psi^{0}_{\mathrm{e'}}(\mathbf{r})\nabla\psi^{0}_{\mathrm{e}}(\mathbf{r})] \quad (37)$$

The corresponding expression for the time-dependent electron probability density is given by

$$\rho_{\mathrm{ev,e'v'}}(\mathbf{r},t) = \int\tilde{\Psi}^{*}_{\mathrm{ev,e'v'}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}},t)\tilde{\Psi}_{\mathrm{ev,e'v'}}(\mathbf{r},\mathbf{R},\dot{\mathbf{R}},t)\,\mathrm{d}\mathbf{R} \quad (38)$$

from which, after substitution of eqs 32 and 33, we obtain the following expression for the time-dependent electron probability density

$$\rho_{\mathrm{ev,e'v'}}(\mathbf{r},t) = 2c_{\mathrm{ev}}c_{\mathrm{e'v'}}O_{\mathrm{ev,e'v'}}(\mathbf{r})\cos\omega_{\mathrm{ev,e'v'}}t \quad (39)$$

where the time-independent TPD, also defined in eqs 9 and 10 above, is given by

$$O_{\mathrm{ev,e'v'}}(\mathbf{r}) = \Bigg\{O^{0}_{\mathrm{ee'}}(\mathrm{r})\langle\phi_{\mathrm{ev}}|\phi_{\mathrm{e'v'}}\rangle + \sum_{A,\alpha}[\sum_{\mathrm{s}\neq\mathrm{e'}}D^{0}_{\mathrm{se'},A\alpha}O^{0}_{\mathrm{es}}(\mathbf{r}) + \sum_{\mathrm{s}\neq\mathrm{e}}D^{0}_{\mathrm{se},A\alpha}O^{0}_{\mathrm{e's}}(\mathbf{r})]\langle\phi_{\mathrm{ev}}|R_{A\alpha}|\phi_{\mathrm{e'v'}}\rangle + \sum_{A,\alpha}\left[\sum_{\mathrm{s}\neq\mathrm{e'}}\frac{D^{0}_{\mathrm{se'},A\alpha}O^{0}_{\mathrm{es}}(\mathbf{r})}{\omega^{0}_{\mathrm{se'}}} - \sum_{\mathrm{s}\neq\mathrm{e}}\frac{D^{0}_{\mathrm{se'},A\alpha}O^{0}_{\mathrm{e's}}(\mathbf{r})}{\omega^{0}_{\mathrm{se'}}}\right]\langle\phi_{\mathrm{ev}}|\mathrm{i}\dot{R}_{A\alpha}|\phi_{\mathrm{e'v'}}\rangle\Bigg\} \quad (40)$$

and where the pure electronic TPD is given simply by

$$O^{0}_{\mathrm{ee'}}(\mathrm{r}) = \psi^{0}_{\mathrm{e}}(\mathbf{r})\psi^{0}_{\mathrm{e'}}(\mathbf{r}) \quad (41)$$

From these expressions, it can be seen that in eqs 36 and 40 the BO nuclear-position-dependent terms contribute with opposite relative signs compared to the non-BO nuclear-velocity-dependent terms. For the TCD in eq 36, the non-BO terms reinforce and the BO terms tend to cancel, while the reverse is the case for the TPD in eq 40.

The relative sizes of the *individual* BO and non-BO contributions, apart from their relative signs as just discussed, are approximately the ratio of the energy spacings of vibrational levels v and v′, compared to that of electronic levels e or e′ and s. This can be seen by comparing corresponding BO and non-BO terms in either eq 36 or 40 and noting that the vibrational matrix elements of the nuclear velocity operator carry a vibrational frequency dependence relative to the corresponding matrix element of the nuclear position operator (see eq 49 below). Thus individual non-BO terms are smaller than the corresponding BO terms unless the electronic energy level spacing approaches the spacing of vibrational levels. This is the standard criterion for the breakdown of the BO approximation. However, the net relative importance of these terms in these expressions depends on whether the probability density or the current density is being calculated. In the case of probability density, the BO terms tend to dominate and for current density, the non-BO terms are generally more important. As shown below, in the limiting case of vibrational transitions, the TPD to first order depends only on BO terms whereas the TCD depends only on non-BO terms.

3. Conservation of Probability and Current Density. The conservation equation for TCD and TPD is satisfied in the general case of a vibronic transition between states ev and e′v′ as given by the wave function in eq 33, before approximations are invoked, by direct analogy to eqs 7−15. Conservation also holds for pure electronic TCD and TPD given by eqs 37 and 41, respectively, for the same reason. Exact conservation is not apparent in the case of vibronic transitions using vibronic wave functions approximated by first-order perturbation theory and in the more special case of the CA approximation. Algebraic complexities arise when two quantum numbers, *e* and *v*, change independently, leading to more than one harmonic frequency and more than one transition matrix within the same expressions for TPD and TCD. As we show below, the exact algebraic conservation is restored for the case of pure vibrational transitions where the electronic quantum number does not change.

Transition Current Density in Pure Vibrational Transitions

An important limit of the TCD and TPD expressions for a vibronic transition is the case of pure vibrational transitions within a single electronic state. If state e′ is set equal to e, then from eqs 36 and 40 the expressions for pure vibrational

TCD and TPD, respectively, are given by

$$\mathbf{J}_{\mathrm{ev,ev'}}(\mathbf{r}) = 2\sum_{A,\alpha}\left[\sum_{\mathrm{s}\neq\mathrm{e}}\frac{D^{0}_{\mathrm{se},A\alpha}\mathbf{J}^{0}_{\mathrm{es}}(\mathbf{r})}{\omega^{0}_{\mathrm{se}}}\right]\langle\phi_{\mathrm{ev}}|\mathrm{i}\dot{R}_{A\alpha}|\phi_{\mathrm{ev'}}\rangle \tag{42}$$

$$O_{\mathrm{ev,ev'}}(\mathbf{r}) = 2\sum_{A,\alpha}[\sum_{\mathrm{s}\neq\mathrm{e}}D^{0}_{\mathrm{se},A\alpha}O^{0}_{\mathrm{es}}(\mathbf{r})]\langle\phi_{\mathrm{ev}}|R_{A\alpha}|\phi_{\mathrm{ev'}}\rangle \tag{43}$$

From these equations it is clear that electron TCD associated with nuclear, vibrational motion is governed solely by non-BO nuclear velocity contributions and that the corresponding TPD is governed by BO nuclear position contributions. This means that pure vibrational TCD is induced by nuclear velocities and formally lies outside the BO approximation but that the redistribution of probability density due to nuclear displacements, and caused by the TCD, is described within the BO approximation.

1. Conservation of Vibrational Electronic Current Density. We can demonstrate the close relation between nuclear-velocity-induced electron current density and nuclear-position-induced changes in electron probability density through the application of the continuity equation given in general terms by eq 12. For pure vibrational transitions we have

$$-\nabla\cdot\mathbf{j}_{\mathrm{ev,ev'}}(\mathbf{r},t) = \frac{\partial\rho_{\mathrm{ev,ev'}}(\mathbf{r},t)}{\partial t} \tag{44}$$

where the time-dependent densities from eqs 35 and 39, respectively, are given by

$$\mathbf{j}_{\mathrm{ev,ev'}}(\mathbf{r},t) = 4c_{\mathrm{ev}}c_{\mathrm{ev'}}\sum_{A,\alpha}\left[\sum_{\mathrm{s}\neq\mathrm{e}}\frac{D^{0}_{\mathrm{se},A\alpha}\mathbf{J}^{0}_{\mathrm{es}}(\mathbf{r})}{\omega^{0}_{\mathrm{se}}}\right]\langle\phi_{\mathrm{ev}}|\mathrm{i}\dot{R}_{A\alpha}|\phi_{\mathrm{ev'}}\rangle\sin\omega_{\mathrm{ev,ev'}}t \tag{45}$$

$$\rho_{\mathrm{ev,ev'}}(\mathbf{r},t) = 4c_{\mathrm{ev}}c_{\mathrm{ev'}}\sum_{A,\alpha}[\sum_{\mathrm{s}\neq\mathrm{e}}D^{0}_{\mathrm{se},A\alpha}O^{0}_{\mathrm{es}}(\mathbf{r})]\langle\phi_{\mathrm{ev}}|R_{A\alpha}|\phi_{\mathrm{ev'}}\rangle\cos\omega_{\mathrm{ev,ev'}}t \tag{46}$$

Applying the negative gradient to eq 42 and the time-derivative to eq 43, we obtain

$$-\nabla\cdot\mathbf{j}_{\mathrm{ev,e'v'}}(\mathbf{r},t) = -4c_{\mathrm{ev}}c_{\mathrm{ev'}}\sum_{A,\alpha}\left[\sum_{\mathrm{s}\neq\mathrm{e}}\frac{D^{0}_{\mathrm{se},A\alpha}\nabla\cdot\mathbf{J}^{0}_{\mathrm{es}}(\mathbf{r})}{\omega^{0}_{\mathrm{se}}}\right]\langle\phi_{\mathrm{ev}}|\mathrm{i}\dot{R}_{A\alpha}|\phi_{\mathrm{ev'}}\rangle\sin\omega_{\mathrm{ev,e'v'}}t \tag{47}$$

$$\frac{\partial\rho_{\mathrm{ev,e'v'}}(\mathbf{r},t)}{\partial t} = -4c_{\mathrm{ev}}c_{\mathrm{ev'}}\omega_{\mathrm{ev,ev'}}\sum_{A,\alpha}[\sum_{\mathrm{s}\neq\mathrm{e}}D^{0}_{\mathrm{se},A\alpha}O^{0}_{\mathrm{es}}(\mathbf{r})]\langle\phi_{\mathrm{ev}}|R_{A\alpha}|\phi_{\mathrm{ev'}}\rangle\sin\omega_{\mathrm{ev,ev'}}t \tag{48}$$

and if we convert the velocity form of the vibrational integral in eq 47 to the position form using the well-known hypervirial equation

$$\langle\phi_{\mathrm{ev}}|\dot{R}_{A\alpha}|\phi_{\mathrm{ev'}}\rangle = \mathrm{i}\omega_{\mathrm{ev,ev'}}\langle\phi_{\mathrm{ev}}|R_{A\alpha}|\phi_{\mathrm{ev'}}\rangle \tag{49}$$

and use the continuity equation for pure electronic TCD and TPD, given in general form in eq 15, namely,

$$-\nabla\cdot\mathbf{J}^{0}_{\mathrm{es}}(\mathbf{r}) = \omega^{0}_{\mathrm{se}}O^{0}_{\mathrm{es}}(\mathbf{r}) \tag{50}$$

we can write eq 47

$$-\nabla\cdot\mathbf{j}_{\mathrm{ev,e'v'}}(\mathbf{r},t) = -4c_{\mathrm{ev}}c_{\mathrm{ev'}}\omega_{\mathrm{ev,ev'}}\sum_{A,\alpha}[\sum_{\mathrm{s}\neq\mathrm{e}}D^{0}_{\mathrm{se},A\alpha}O^{0}_{\mathrm{es}}(\mathbf{r})]\langle\phi_{\mathrm{ev}}|R_{A\alpha}|\phi_{\mathrm{ev'}}\rangle\sin\omega_{\mathrm{ev,e'v'}}t \tag{51}$$

in exact equality with eq 48 and hence verifying the continuity equation in eq 44.

Discussion

For bound, stationary states of molecules, there are nonzero electron probability densities as well as changes of probability densities between two different stationary states. On the other hand, as we have shown, the electron current density vanishes at every point in the space of the molecule for a single bound stationary state. This fact has prevented extensive use of electron current density for visualizing the nature of unperturbed electronic and vibrational states in molecules.

The limitation is circumvented if we consider two-state properties associated with the coupling of two stationary states by a perturbation. In this case, the two states beat against one another at their difference frequency, setting up nonzero time-dependent oscillations of both electron probability density and electron current density. We have defined the time-independent amplitude of these probability and current density oscillations as the transition probability density, TPD, and the transition current density, TCD, respectively.

In this paper we have extended the theory of electron TCD and TPD to molecular transitions involving nuclear motion in vibronic transitions, in general, and pure vibrational transitions, in particular. The theory of TCD and TPD in vibronic transitions is carried out through first order in nuclear displacement and momentum (velocity), and it is found that both BO and non-BO terms contribute, although differently, to both the TPD and TCD. For pure vibrational transitions, this mixing of BO and non-BO contributions gives way to only BO terms for the TPD and non-BO terms for the TCD. One of the most pleasing results of the theory of TPD and TCD for pure vibrational (nuclear) transitions within a single electronic state is the way the pure BO contributions in TPD join forces with the non-BO contributions in TCD to satisfy exactly the continuity equation for the conservation of charge and current density. In the present formulation, the vibrational TCD is composed of an energy-weighted sum of the product of the vibrational coupling integral and the pure electronic TCDs of the excited states of the molecule.

The derivation of TCD and TPD through time dependent expressions for the electron probability density and current density, respectively, eqs 8 and 10, reveals a fundamental relationship between these two density functions. Both are associated with the internal oscillations that take place in a nonsteady stationary state comprised of two stationary states. They occur in- and out-of-phase (sine and cosine) with respect to one another during the quantum beat oscillations. The TPD is associated with the extremes of electron probability *displacement* away from equilibrium and the TCD is associated with the extremes of electron probability *velocity*, or current density, at the zero displacement position. TPD is the static representation of the oscillation and TCD is the dynamic representation.

This description of densities oscillating in- and out-of-phase is most clear for vibrational transitions where the TCD represents the electron current density that follows the nuclear velocities and similarly TPD that follows nuclear displacements. Each is out of phase with respect to the other in a cycle of harmonic motion at the transition frequency. The analogy carries over clearly to pure electronic transitions where the electron TCD is a vector field representing the dynamics of the oscillation of electron probability for electronic transitions in the same way that electron currents follow nuclear velocities during the motion associated with vibrational transitions. Since there is no restriction on the pairs of states that can be represented with TCD, it should be possible to view the oscillations associated with higher level vibrational transitions, such as overtones and combination bands. It may also be interesting to view the electron TCDs associated with vibronic transitions in which there are changes of both electronic and vibrational quantum states.

Although we have not done so in this paper, it is straightforward to extend the concept of TCD to the motion of the nuclei as well. For vibrational transitions, this would just lead to representations of nuclear velocity vector fields that would take into account the quantum description of the location of the nuclei in molecules. The nonzero nuclear vector fields would be highly localized and would coincide closely with the classical positions and velocities of the nuclei.

In section 3 of the Transition Current Density in Vibronic Transitions section, we pointed out that the integral of the TCD is closely related to the velocity electric-dipole transition moment between the two quantum states. It is important to realize that TCDs are nonzero and well-defined for any pair of quantum states whether or not the transition between the two states is electric-dipole allowed. If it is electric-dipole forbidden, then the integral over space of the TCD vanishes by symmetry, but nevertheless, strong TCD throughout the molecule can be calculated and plotted to see the nature of the electron oscillatory currents for higher multipoles that are set in motion due to the coupling of the two states.

The use of TCDs to visualize the vector fields associated with electron currents set up during transitions in molecules is a powerful new approach to understanding the dynamic nature of electronic motion in all classes of changes of molecular quantum states. The simplest examples are changes in pure electronic states, vibronic states, pure vibrational states, rotational states, and so forth for similar combinations of changes of quantum state.

We have carried out calculations of TCD for pairs of pure electronic states[12] and pure vibrational states.[13] Besides the expected current densities associated with the principal allowed nature of the transition, for example *x*- or *z*-allowed electric dipole transitions, there are interesting current effects off the main current path, which by symmetry may integrate to zero when calculating a molecular transition property, such as electric-dipole absorption strength. Another interesting effect, particularly in transitions with some magnetic-dipole character, is the current density associated with the circulation of charge density. Since circulation need not lead to changes in TPD, the effects of such currents are silent and can be only be seen by calculating the TCD.

TCDs may be used to compare differences between quantum mechanical calculations of transition properties associated with pairs of states. Since the experimental observable for virtually all quantum mechanical states is a property associated with a transition between two states, TCD is a fundamental way to visualize the results of such calculations and to investigate the fundamental nature, in spatial detail, of the electronic motions associated with these transitions.

One can also consider current density associated with reactions between two docked molecules, where the initial and final states correspond to the electronic states of the reactant and product molecules. For electron transfer reactions, the transition current density associated with this single quantum mechanical process can be visualized using this formalism. In cases where long-range electron transfer in biological molecules occurs as a single quantum mechanical transition, TCDs may be calculated from the initial and final states to visualize this process and thereby to gain a better understanding of the relative importance of various "electron pathways". This topic has been considered with the objective of calculating the probability of transitions between initial and final state wave functions, but electron pathways were not explicitly considered.[14,15] An alternative approach is to use path integral simulations to calculate the behavior of an excess electron propagated through π-orbitals as a means to understanding long-range electron transfer in biological molecules.[16]

A related application of TCD is to visualize the electronic and vibrational motion of electrons in molecules that conduct current. Examples are conducting organic crystals or polymers[17−19] and chemical switches that permit the flow of electronic excitation from one part of a molecule to another.[20] TCD can also be considered as a visual, theoretical tool in the emerging field of molecular electronics where molecular fragments can serve as electronic components, such as molecular switches[20] and wires,[21] in the fabrication of molecular level ensembles of devices of various kinds.

Conclusions

We have shown that the theory of TCD and TPD in molecules can be extended to include vibrational motion. For vibronic transitions, the theory is relatively complex and involves the appearance of both BO and non-BO contributions to the TPD and the TCD. For pure vibrational transitions, the theory simplifies such that, to first order in the nuclear position and momentum, only BO terms contribute to the TPD and only non-BO terms contribute to TCD. Through the continuity equation we see that TPD and TCD are nuclear-static and nuclear-dynamic densities associated closely with the oscillations of electron densities during vibrational motion. These two types of oscillation are out of phase, since the oscillations of TPD peak at the extremes of nuclear displacement, and are correlated with nuclear displacements, whereas the TCD peaks at the equilibrium nuclear positions where the nuclear velocities are at their maxima.

TCD is a unique, fundamental way to visualize vector fields associated with all classes of transitions between stationary quantum states in molecules. It appears, therefore, that the potential for TCD to aid our understanding of the electronic motions during such changes of states molecules is quite high. This potential is further enhanced by the rapidly growing power of computational chemistry to provide detailed views of electron probability and current density in molecules.

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References and Notes

(1) Hout, R. F.; Pietro, W. H.; Hehre, W. J. *A Pictorial Approach to Molecular Structure and Reactivity*; John Wiley & Sons: New York, 1984.

(2) Bader, R. F. W. *Atoms in Molecules*; Oxford University Press: New York, 1994.

(3) Thieste, D.; Jones, R. D.; Callis, P. R. *Chem. Phys. Lett.* **1987**, *133*, 14.

(4) Schiff, L. I. *Quantum Mechanics*, 3rd ed.; McGraw-Hill: New York, 1968.

(5) Levin, I. N. *Quantum Mechanics*, 3rd ed.; Allyn and Bacon: Boston, 1983.

(6) Nafie, L. A. In *Molecular and Biomolecular Electronics*; Birge, R. R., Ed.; American Chemical Society: Washington, D.C., 1994; Vol. 240, pp 63−80.

(7) Nafie, L. A. *J. Chem. Phys.* **1983**, *79*, 4950−4957.

(8) Nafie, L. A. *J. Chem. Phys.* **1992**, *96*, 5687−5702.

(9) McWeeny, R. *Methods of Molecular Quantum Mechanics*; Academic Press: New York, 1989; p 128.

(10) Buckingham, A. D.; Fowler, P. W.; Galwas, P. A. *Chem. Phys.* **1987**, *112*.

(11) Buckingham, A. D. *Faraday Discuss.* **1994**, *99*, 1−12.

(12) Freedman, T. B.; Shih, M.-L.; Nafie, L. A. To be submitted.

(13) Freedman, T. B.; Shih, M.-L.; Lee, E.; Nafie, L. A. *J. Am. Chem. Soc.,* submitted.

(14) Beratan, D. N.; Onuchic, J. N.; Hopfield, J. J. *J. Chem. Phys.* **1985**, *83*, 5325−5329.

(15) Beratan, D. N.; Onuchic, J. N.; Hopfield, J. J. *J. Chem. Phys.* **1987**, *86*, 4488−4498.

(16) Wheeler, R. A.; McCammon, J. A. *Chem. Phys. Lett.* **1990**, *174*, 369−376.

(17) Gussoni, M.; Castiglioni, C.; Zerbi, G. In *Spectroscopy of Advanced Materials*; Clark, R. J. H., Hester, R. E., Eds.; John Wiley and Sons: New York, 1991; Vol. 19, p 251.

(18) Castiglioni, C.; Gussoni, M.; Zoppo, M. D.; Zerbi, G. *Solid State Commun.* **1992**, *82*, 13−17.

(19) Zoppo, M. D.; Castiglioni, C.; Veronelli, M.; Zerbi, G. *Synth. Met.* **1993**, *55*, 3919.

(20) Wagner, R. W.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 3996.

(21) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759.