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Electron Tunneling in Quasi-One-Dimensional Resonant Molecular Systems. Ab Initio Study

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The method of tunneling currents is applied for study of electron-tunneling dynamics in quasi-one-dimensional donor−bridge−acceptor systems in which the bridge is composed of a sequence of atoms located on a straight line connecting donor and acceptor complexes. Such a system provides a simple model for the description of electronic processes in molecular wires. Of our particular interest are the following questions: how exactly does an electron tunnel through an atom or a molecule, and what is the precise meaning of "through-bond" and "through-space" tunneling, the concepts frequently used in the description of electron tunneling in proteins. Our method consists of an ab initio electronic structure calculation of the spatial distribution of tunneling currents occurring during the tunneling transition in the system, when an electron tunnels from the one end of molecular wire to the other. The analysis is based on calculation of two diabatic electronic states corresponding to localization of a tunneling electron on donor and acceptor sites, respectively. All electrons in the system are taken into account at the Hartree−Fock level, and as such the method allows us to examine the reaction of the valence electrons on the bridge to the tunneling charge. The symmetry of the chosen system allows a relatively simple way for a complete and detailed analysis of the spatial distribution of the currents in the system. These results provide new insights into the nature of long-distance electron tunneling in organic media.

Introduction

Long-distance tunneling is a critical step in electron-transfer reactions in many donor−bridge−acceptor systems. Important examples include, for example, electron transfer in proteins,[1−5] electron tunneling in molecular monolayers in STM experiments,[6−8] and electronic processes in molecular assemblies that are studied as prototypes of molecular electronic devices.[9] A concept of molecular wire is often used in molecular electronics studies[10] when referring to a single, usually long, molecule connecting distant donor and acceptor complexes that exchange an electron in thermal or photoexcited reactions. The nature of electron transport in such systems is of great universal interest, and it has therefore been the subject of active experimental and theoretical studies in the past.

The fundamental principles of long-distance electronic coupling in molecular bridged systems were discovered in the early 1960s.[11] In the most common case, donor and acceptor localized electronic states are the only states that are mixed as the reaction proceeds; i.e., there are no other states that ever get resonant with these two. An electron therefore can reside on either the donor or the acceptor states, and all intermediate states for a tunneling electron are virtual. (This is by no means the only possible mechanism for long-distance charge transfer; for discussion of other models see, e.g., ref 12.) The mixing occurs, according to fundamental postulates of electron-transfer theory,[13,14] when donor and acceptor states are brought into resonance in a suitable thermal fluctuation of nuclear coordinates of the system and because of the nonzero quantum mechanical coupling of two states. This coupling, however, is not direct, since electronic orbitals of donor and acceptor complexes do not overlap, but instead there is a sequence of overlapping orbitals owing to bridging atoms that results in an effective or superexchange coupling.

The absence of intermediate resonances and sequential nature of the coupling of virtual bridging states makes the process of electron exchange in such a case essentially equivalent to semiclassical tunneling.

In recent years detailed experimental studies of biological electron transfer have stimulated advanced theoretical analysis of long-distance electron tunneling (see e.g., recent review in ref 15 and references therein). As a result, the fundamental idea of superexchange electronic coupling of distant donor and acceptor complexes has now acquired a remarkable degree of sophistication. Current theories are able to account for structural and dynamical[16] features of the bridging medium between donor and acceptor at the level of individual atoms and provide the basis for quantitative analysis of structure−function analysis of electron-transfer proteins.[15]

Most of the theories of electron transfer in proteins, however, are based on a one-electron picture, owing to the enormous complexity of the problem.[15,17−33] Smaller systems, on the other hand, have been successfully studied using the many-electron quantum chemistry approach,[34−37] and currently efforts are underway to develop many-electron theories for proteins.[38]

In refs 39 and 40, the method of interatomic tunneling currents for the description of long-range electron transfer in proteins was introduced. This theory provides an efficient solution both for the problem of finding which atoms in the intervening medium between donor and acceptor, and to what extent, are important in the tunneling process (tunneling pathways), and for the problem of evaluation of the magnitude of superexchange tunneling matrix element (electronic coupling) for bridge-

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mediated electron-transfer reactions. In a recent work,[41] the formulation of the theory was extended to include the many-electron description.

The method of atomic currents can be applied for the analysis of electron tunneling in proteins, such as Ru-modified blue copper azurin and cytochrome molecules from recent experimental studies of Gray and co-workers,[4,5] or for the description of electron transfer in molecular monolayers in STM experiments.[6−8] The structure of the tunneling flow in the intervening medium at the atomic level of resolution can provide an important insight into the details of the mechanism of long-distance tunneling.

In this paper the method of tunneling currents is applied for study of electron-tunneling dynamics in quasi-one-dimensional donor−bridge−acceptor systems that provide a model for the description of electronic processes in molecular wires. Of our particular interest are the following questions: how exactly does an electron tunnel through an atom or a molecule, and what is the precise meaning of "through-bond" and "through-space" tunneling, the concepts frequently used in the description of electron tunneling in proteins. Our method consists of an ab initio electronic structure calculation of the spatial distribution of tunneling currents occurring during the tunneling transition in the system, when an electron tunnels from the one side of the molecular wire to the other. The analysis is based on calculation of two diabatic electronic states corresponding to localization of a tunneling electron on donor and acceptor sites, respectively. All electrons in the system are taken into account at the Hartree−Fock level, and as such the method allows us to examine the reaction of the valence electrons on the bridge to the tunneling charge. The symmetry of the chosen system allows a relatively simple way for a complete and detailed analysis of the spatial distribution of the currents in the system. The results reported below provide new insights into the nature of long-distance electron tunneling in organic media. Also, using the method described in this paper, the quality of the one-electron approximation can be evaluated quantitatively.

The paper is structured as follows. In the next section we introduce and discuss many-electron density and current density operators and show how tunneling dynamics can be analyzed with these operators. In section 3 main approximations employed in the calculation of donor and acceptor wave functions are discussed. In section 4 examples of calculations of tunneling currents in various model systems are presented. Section 5 closes the paper with some additional discussion and conclusions.

2. Current Density in a Tunneling Transition

2.1. Current Density Operator. The current density of N classical particles with coordinates $x_i(t)$ moving with velocities $v_i(t) = \dot{x}_i(t)$ is given by

$$j(x) = \sum_i^N \delta(x - x_i) v_i \tag{2.1}$$

The quantum generalization of the above equation results in the following expression for the *operator* of current density

$$\hat{j}(x) = \frac{1}{2}\sum_i^N \left[\delta(x - x_i)\frac{\hat{p}_i}{m} + \frac{\hat{p}_i^+}{m}\delta(x - x_i)\right] \tag{2.2}$$

where m is the mass of particles, electrons in our case, and $\hat{p}_i$ is the momentum operator of the ith electron, $-i\hbar\partial/\partial x_i$. The hermitian symmetrization of the classical expression makes the current density operator hermitian. The hermitian conjugated operator $\hat{p}_i^+$ is assumed to be acting on the left. The total coordinate representation of the above expression thus has the following form:

$$\hat{j}(x) = \frac{\hbar}{2mi}\sum_i^N \left[\delta(x - x_i)\frac{\partial}{\partial x_i} - \frac{\partial^+}{\partial x_i}\delta(x - x_i)\right] \tag{2.3}$$

Thus, the current density has the form of a one-electron operator. In the same representation the electron density operator reads

$$\hat{\rho}(x) = \sum_i^N \delta(x - x_i) \tag{2.4}$$

which is a one-electron operator as well. We can now apply the standard technique to calculate matrix elements of these operators for many-electron wave functions.

In ref 41 the second quantization method was used for the analysis of tunneling currents. It can be shown that the above operators and the current density operator discussed in ref 41 are the same. For example, applying the standard technique of the field operators $\hat{\psi}(x)$ and $\hat{\psi}^+(x)$ (see, e.g., ref 42) the above operators can be rewritten in second-quantized form as

$$\hat{\rho}(x) = \hat{\psi}_\sigma^+(x)\,\hat{\psi}_\sigma(x) \tag{2.5}$$

and

$$\hat{\vec{j}}(x) = \frac{\hbar}{2mi}(\hat{\psi}_\sigma^+(x)\nabla\hat{\psi}_\sigma(x) - \hat{\psi}_\sigma^+(x)\nabla^+\hat{\psi}_\sigma(x)) \tag{2.6}$$

where summation is assumed over the repeating spin index σ. Thus, the current density discussed in this paper and in ref 41 are the same; however, the mathematical formalism of second quantization required for treatment of the above expressions is quite different from that of the present paper.

2.2. Tunneling Dynamics in Terms of $\vec{J}(x)$. The idea of our method is to examine spatial distribution of the current density in a tunneling transition. Suppose two resonant diabatic electronic states $|\mathrm{D}\rangle$ and $|\mathrm{A}\rangle$ corresponding to localization of the tunneling electron on the donor and on the acceptor complexes, respectively,[34] are coupled by the transfer matrix element[34]

$$T_{\mathrm{DA}} = \frac{\langle \mathrm{D}|H|\mathrm{A}\rangle - E_0 S_{\mathrm{DA}}}{(1 - S_{\mathrm{DA}}^2)} \tag{2.7}$$

where H is many-electron Hamiltonian of the system at fixed nuclear coordinates, $S_{\mathrm{DA}} = \langle \mathrm{D}|\mathrm{A}\rangle$ is the overlap of the two states, and $E_0 = \langle \mathrm{D}|H|\mathrm{D}\rangle = \langle \mathrm{A}|H|\mathrm{A}\rangle$ is a common resonance energy of states D and A. It is assumed that all other electronic states are far from D and A states in energy, so that only two states are involved in mixing and in dynamics.

Then, if initially the tunneling electron is localized in the donor state, $|\mathrm{D}\rangle$, later in time the total electronic wave function will evolve into a linear combination of states $|\mathrm{D}\rangle$ and $|\mathrm{A}\rangle$ as follows

$$|\Psi(t)\rangle = \cos(T_{\mathrm{DA}}t/\hbar)|\mathrm{D}\rangle - i\,\sin(T_{\mathrm{DA}}t/\hbar)|\mathrm{A}\rangle \tag{2.8}$$

We wish to examine current density and electron density in such a state. For local density we find

$$\rho(x, t) = \langle\Psi(t)|\hat{\rho}(x)|\Psi(t)\rangle = \cos^2(\theta)\,\langle \mathrm{D}|\hat{\rho}(x)|\mathrm{D}\rangle + \sin^2(\theta)\,\langle A|\hat{\rho}(x)|A\rangle \quad (2.9)$$

where

$$\theta = \frac{T_{\mathrm{DA}}}{\hbar}t \quad (2.10)$$

The local density changes in time as follows:

$$\frac{\partial\rho(x, t)}{\partial t} = \frac{T_{\mathrm{DA}}}{\hbar}(\langle \mathrm{A}|\hat{\rho}(x)|\mathrm{A}\rangle - \langle \mathrm{D}|\hat{\rho}(x)|\mathrm{D}\rangle)\sin 2\theta \quad (2.11)$$

On the other hand, the local current density in the same state is

$$\vec{j}(x, t) = \langle\Psi(t)|\hat{\vec{j}}(x)|\Psi(t)\rangle = i\langle A|\hat{\vec{j}}(x)|D\rangle \sin 2\theta \quad (2.12)$$

As expected, both density and local current are changing in time periodically with the same frequency $2T_{\mathrm{DA}}/\hbar$.

In both expressions the time dependence is defined by the factor sin 2θ. The rest of the expression gives an amplitude of oscillation, which as a function of coordinates gives a spatial distribution of the current/density in the whole system. Using the same notation as in one-electron theory, the spatial part of the current, $\vec{J}(x)$, is introduced as follows:

$$\vec{j}(x, t) = -\vec{J}(x)\sin 2\theta \quad (2.13)$$

Given this definition, the spatial distribution is

$$\vec{J}(x) = -i\langle \mathrm{A}|\hat{\vec{j}}(x)|\mathrm{D}\rangle \quad (2.14)$$

Using the conservation equation for current

$$\frac{\partial\hat{\rho}(x)}{\partial t} = -\mathrm{div}\,\hat{\vec{j}}(x) \quad (2.15)$$

and the expressions for $\rho(x, t)$ and $\vec{j}(x, t)$, we find a relation between local density and current density in a tunneling system:

$$\frac{T_{\mathrm{DA}}}{\hbar}(\langle \mathrm{A}|\hat{\rho}(x)|\mathrm{A}\rangle - \langle \mathrm{D}|\hat{\rho}(x)|\mathrm{D}\rangle) = \mathrm{div}\,\vec{J}(x) \quad (2.16)$$

Finally, surrounding the donor complex by some closed surface S_{D} that will run sufficiently far from it so as to include most of the charge density corresponding to tunneling electron on the donor site and integrating the above eq 2.16 over the volume comprised by S_{D}, one finds a a useful relation between tunneling matrix element and current density:

$$T_{\mathrm{DA}} = -\hbar\int_{S_{\mathrm{D}}} \mathrm{d}\vec{s}\;\vec{J}(x) \quad (2.17)$$

The same relation was found before in one-electron approximation.[39,40] Equations 2.14 and 2.17 are most important relations of this section that are used in our calculations described in the following sections.

2.3. Calculation of $\vec{J}(x)$. Suppose states $|\mathrm{D}\rangle$ and $|\mathrm{A}\rangle$ are one-determinant many-electron functions, which are written in terms of (real) molecular orbitals $\varphi^{\mathrm{D}}_{i\sigma}$ and $\varphi^{\mathrm{A}}_{i\sigma}$ with corresponding spin orbitals $\chi^{\mathrm{D}}_{i\sigma}$ and $\chi^{\mathrm{A}}_{i\sigma}$, where σ is the spin index, $\sigma = \alpha$, β. These orbitals are the optimized orbitals obtained from Hartree−Fock (HF) calculations of states D and A. The D and A states then have the following form:

$$|\mathrm{D}\rangle = |\chi^{\mathrm{D}}_{1\alpha}\cdots\chi^{\mathrm{D}}_{p\alpha}\chi^{\mathrm{D}}_{1\beta}\cdots\chi^{\mathrm{D}}_{q\beta}\rangle \quad (2.18)$$

$$|\mathrm{A}\rangle = |\chi^{\mathrm{A}}_{1\alpha}\cdots\chi^{\mathrm{A}}_{p\alpha}\chi^{\mathrm{A}}_{1\beta}\cdots\chi^{\mathrm{A}}_{q\beta}\rangle \quad (2.19)$$

Using standard rules for matrix elements of one-electron operators,[43] we have

$$\langle \mathrm{A}|\sum_i \hat{O}(i)|\mathrm{D}\rangle = \det(\mathbf{S}_{\mathrm{AD}})\sum_{ij,\sigma}(\mathbf{S}^{-1}_{\mathrm{AD}})_{i\sigma,j\sigma}\langle\varphi^{\mathrm{A}}_{j\sigma}|\hat{O}|\varphi^{\mathrm{D}}_{i\sigma}\rangle \quad (2.20)$$

for any operator $\hat{O}$ of the form of eq 2.3 or eq 2.4. The overlap matrix $\boldsymbol{S}_{\mathrm{AD}}$ in the above equation is given by

$$(\mathbf{S}_{\mathrm{AD}})_{i\sigma,j\lambda} = \langle\chi^{\mathrm{A}}_{i\sigma}|\chi^{\mathrm{D}}_{j\lambda}\rangle = \delta_{\sigma\lambda}\langle\varphi^{\mathrm{A}}_{i\lambda}|\varphi^{\mathrm{D}}_{j\lambda}\rangle \quad (2.21)$$

The determinant of this matrix is the overlap integral for states A and D:

$$S_{\mathrm{AD}} = \langle \mathrm{A}|\mathrm{D}\rangle = \det(\mathbf{S}_{\mathrm{AD}}) \quad (2.22)$$

Much computational simplification in the evaluation of the matrix elements of the form of eq 2.20 is gained if molecular orbitals $\varphi^{\mathrm{A}}_{i\sigma}$ and $\varphi^{\mathrm{D}}_{i\sigma}$ of corresponding spin orbitals are biorthogonalized.[44−47] In this case the overlap matrix of states A and D is diagonal

$$\langle\varphi^{\mathrm{A}}_{i\sigma}|\varphi^{\mathrm{D}}_{j\sigma}\rangle = \delta_{ij}s^{\sigma}_i, \quad (2.23)$$

and for states with p orbitals in α spin and q orbitals in β spin

$$\det(\mathbf{S}_{\mathrm{AD}}) = \prod_i^p s^{\alpha}_i \prod_j^q s^{\beta}_j \quad (2.24)$$

and

$$(\mathbf{S}^{-1}_{\mathrm{AD}})_{i\sigma,j\sigma} = \delta_{ij}(s^{\sigma}_i)^{-1}, \quad \sigma = \alpha, \beta \quad (2.25)$$

Using the above results and substituting current operator eq 2.3 for $\hat{O}$ in eq 2.20 we find the following explicit form for spatial part of the current $\vec{J}(x)$ defined in eq 2.14:

$$\vec{J}(x) = -\frac{\hbar}{2m}\det(\mathbf{S}_{\mathrm{AD}})\sum_{i,\sigma}\frac{1}{s^{\sigma}_i}(\varphi^{\mathrm{A}}_{i\sigma}(x)\nabla\varphi^{\mathrm{D}}_{i\sigma}(x) - \varphi^{\mathrm{D}}_{i\sigma}(x)\nabla\varphi^{\mathrm{A}}_{i\sigma}(x)) \quad (2.26)$$

This expression is an obvious generalization of the one-electron picture. Different pairs of orbitals contribute to current density. If molecular orbitals in states D and A are biorthogonalized, as we assumed above, currents of pairs of corresponding (overlapping) orbitals of donor and acceptor states contribute to current density. The smaller the overlap between corresponding orbitals in donor and acceptor wave functions (i.e., the greater the change of an orbital in D and A states), the greater the contribution of a given pair of orbitals. In most of the cases (but not in all), it should be expected that only one orbital will be significantly different in donor and acceptor states and an electron occupying these orbitals in the initial and final states of the system will give most of the contribution to the current. It does not mean, however, that other electrons are not important. First of all, other electrons will give some direct contribution owing to electron relaxation effects—their orbitals will be shifted to some degree owing to polarization effects—and also other electrons contribute most strongly indirectly since the important orbitals are determined self-consistently by all other electrons in the system. Finally, many electrons can contribute to current owing to the exchange effects.

We can now express the currents in terms of the atomic basis functions of which molecular orbitals are built. Each of the molecular orbitals are assumed to be found in a HF calculation as a linear combination of atomic basis set functions ϕ_μ

$$\varphi^{\mathrm{D}}_{i\sigma} = \sum_{\mu}^{K} \mathrm{D}^{\sigma}_{\mu i}\phi_{\mu}, \tag{2.27}$$

$$\varphi^{\mathrm{A}}_{j\sigma} = \sum_{n}^{K} \mathrm{A}^{\sigma}_{\nu j}\phi_{\nu} \tag{2.28}$$

where K is the total number of atomic orbitals in the basis set of the system.

Then, in terms of atomic orbitals the expression for currents takes the following form

$$\vec{J}(x) = -\frac{\hbar}{2m}\det(\mathbf{S}_{\mathrm{AD}})\sum_{\mu\nu,\sigma} B^{\sigma}_{\mu\nu}(\phi_{\mu}(x)\nabla\phi_{\nu}(x) - \phi_{\nu}(x)\nabla\phi_{\mu}(\mathrm{x})) \tag{2.29}$$

where the density matrix $B^{\sigma}_{\mu\nu}$ is defined as follows

$$B^{\sigma}_{\mu\nu} = \sum_{i=1}^{(p,q)} \mathrm{A}^{\sigma}_{\mu i}\frac{1}{s^{\sigma}_{i}}\mathrm{D}^{\sigma}_{\nu i} \tag{2.30}$$

where summations are limited by p for α spin and by q for β spin.

Using antisymmetry of the above expression (eq 2.29) in indices μ and ν, one finds the final expression for currents

$$\vec{J}(x) = \vec{J}_{\alpha}(x) + \vec{J}_{\beta}(x) \tag{2.31}$$

$$\vec{J}_{\alpha}(x) = -\frac{\hbar}{2m}\det(\mathbf{S}_{\mathrm{DA}})\sum_{\mu,\nu=1}^{K}(B^{\alpha}_{\mu\nu} - B^{\alpha}_{\nu\mu})\phi_{\mu}(x)\nabla\phi_{\nu}(x) \tag{2.32}$$

$$\vec{J}_{\beta}(x) = -\frac{\hbar}{2m}\det(\mathbf{S}_{\mathrm{DA}})\sum_{\mu,\nu=1}^{K}(B^{\beta}_{\mu\nu} - B^{\beta}_{\nu\mu})\phi_{\mu}(x)\nabla\phi_{\nu}(x) \tag{2.33}$$

where $\det(\boldsymbol{S}_{\mathrm{DA}})$ is given by eq 2.24 and $B^{\sigma}_{\mu\nu}$ is defined by eq 2.30.

Similarly, the overlap matrices can be expressed in terms of the overlap integrals of the atomic orbitals. These expressions have very simple structure and are directly suitable for programming.

3. Choice of Donor and Acceptor Wave Functions

In this section we discuss the approximations employed in the evaluations of the donor and acceptor wave functions and several related issues of the numerical accuracy of calculations of the tunneling currents.

All of the calculations discussed in this paper were performed on symmetric systems. In such a case there exist two closely lying eigenstates, which we will call ψ_a and ψ_b, with energies E_{a} and E_{b}, respectively. The state with the lowest energy is the ground state. These two states correspond to the usual symmetric and antisymmetric combinations of the donor and acceptor states, and the splitting between the two states is twice the value of the coupling, $\Delta E = |E_{\mathrm{b}} - E_{\mathrm{a}}| = 2|T_{\mathrm{DA}}|$. We assume that other electronic states are much higher in energy than ψ_{a} and ψ_{b}, i.e.

$$\min(E_i - E_{\mathrm{a,b}}) \gg \Delta E \tag{3.1}$$

where E_i are energies of some other (excited) electronic states in the system. It is clear that the condition above can always be satisfied at large distances between donor and acceptor since ΔE decreases exponentially with the distance.

The precise meaning of $|\mathrm{D}\rangle$ and $|\mathrm{A}\rangle$ states is defined by the following equations:

$$|\mathrm{D}\rangle = \frac{|\psi_{\mathrm{a}}\rangle + |\psi_{\mathrm{b}}\rangle}{2^{1/2}} \tag{3.2}$$

$$|\mathrm{A}\rangle = \frac{|\psi_{\mathrm{a}}\rangle - |\psi_{\mathrm{b}}\rangle}{2^{1/2}} \tag{3.3}$$

Thus, we assume that at time $t = 0$ a nonstationary state is created from the two eigenstates of the system. In the systems of our interest the $|\mathrm{D}\rangle$ state will be localized on one end of the molecule and the $|\mathrm{A}\rangle$ state on the other. In the subsequent evolution for $t > 0$, the system will experience quantum beats between states D and A with the frequency $2T_{\mathrm{DA}}/\hbar$, as eq 2.8 states.

We notice that $|\mathrm{D}\rangle$ and $|\mathrm{A}\rangle$ states so defined are exactly orthogonal, owing to orthogonality of *a* and *b* states, and the tunneling matrix element defined by eq 2.7 is given exactly by

$$T_{\mathrm{DA}} = (E_{\mathrm{a}} - E_{\mathrm{b}})/2 \tag{3.4}$$

We assume that E_{a} is the lowest energy and ψ_{a} is symmetric, which means that the tunneling matrix element is negative. If, on the other hand, the antisymmetric state b has the lowest energy, then the tunneling matrix element is positive. The currents defined in the previous section will change direction, which formally corresponds to $|\mathrm{A}\rangle$ being the donor state.

If the states ψ_{a} and ψ_{b} were easily available, then the $|\mathrm{D}\rangle$ and $|\mathrm{A}\rangle$ states could be exactly determined using the above definition. In fact, for symmetric and relatively simple systems, such as in the present discussion, the ground and the first excited state can be found relatively easily. However, in a more general case the states ψ_{a} and ψ_{b} are not available (for a simple reason that the exact configuration of the nuclei and of the external field resulting at the degeneracy of the donor and acceptor states is not known), and the value of the tunneling matrix element cannot be determined using eq 3.4. Hence, in general, the strategy of calculations is to find an approximation for $|\mathrm{D}\rangle$ and $|\mathrm{A}\rangle$ states and then to use eq 2.7 for matrix element evaluation. These approximate states are in general not orthogonal, and there exists a small overlap S_{DA} between them.

In a general case the approximate method of finding $|\mathrm{D}\rangle$ and $|\mathrm{A}\rangle$ states would be to consider two different configurations of the system that correspond to an electron localized on donor and acceptor complexes and then to solve the Schrödinger equation (i.e., to find ground state) separately for both approximate $|\mathrm{D}\rangle$ and $|\mathrm{A}\rangle$ states. Both configurations, of course, should be as close as possible to the actual transition-state configuration. This method is based on the idea that the Hamiltonian of the system in the D configuration will be close to actual Hamiltonian in the region of the donor complex and that of the A configuration will be close to the actual Hamiltonian in the region of the acceptor. Then the approximate wave functions will be close to what one understands intuitively by donor and acceptor electronic states.

The quality of the wave functions in the whole space is an important issue since tunneling matrix elements and tunneling currents are exponentially small and hence are expected to be sensitive to minor changes of the Hamiltonian. We therefore formulate the approximation for $|\mathrm{D}\rangle$ and $|\mathrm{A}\rangle$ states more accurately.

The exact state $|\mathrm{D}\rangle$ defined by eq 3.2 satisfies the following equation

$$H|\mathrm{D}\rangle = (E_{\mathrm{a}}|\psi_{\mathrm{a}}\rangle + E_{\mathrm{b}}|\psi_{\mathrm{b}}\rangle)/2^{1/2} \tag{3.5}$$

which can be written as

$$H|\mathrm{D}\rangle = E_0|\mathrm{D}\rangle + T_{\mathrm{DA}}|\mathrm{A}\rangle \tag{3.6}$$

where E_0 is the midpoint between E_{a} and E_{b}

$$E_{\mathrm{a,b}} = E_0 \pm T_{\mathrm{DA}} \tag{3.7}$$

E_0 is what is usually assumed by the tunneling energy. This energy is negative and usually is of the order of several electronvolts.

In coordinate representation eq 3.6 can be rewritten as follows:

$$\left(H - T_{\mathrm{DA}}\frac{\psi_{\mathrm{A}}(x)}{\psi_{\mathrm{D}}(x)}\right)\psi_{\mathrm{D}}(x) = E_0\psi_{\mathrm{D}}(x) \tag{3.8}$$

The expression in parentheses in the above equation can be viewed as an effective Hamiltonian H_{D} for the function ψ_{D}. It is clear that in the region of the donor ψ_{A} is small, of the order of $|T_{\mathrm{DA}}/E_0|$, while ψ_{D} is large (order of unity in atomic units). T_{DA} itself is very small compared with electronic energies of H, hence the effective Hamiltonian H_{D} for ψ_{D} in the region of the donor site is indeed close to H. Further analysis of simple 1-D models shows that the second term in the effective Hamiltonian can be neglected also in the barrier region, and only in the acceptor well it is of the order of H itself. Hence, the effective Hamiltonian for exact ψ_{D} is significantly different from the original Hamiltonian H only in the acceptor well.

Thus, solving the equation for ψ'_{D} with some effective Hamiltonian H'_{D}, which coincides with, or is very close to, H, everywhere in space except in the acceptor well, can give an accurate representation of the actual ψ_{D} in the region of the donor and under the barrier, however, not in the acceptor well. A similar result can be obtained for the effective Hamiltonian H'_{A} and for an approximate function ψ'_{A}.

In our calculations and in earlier work of Newton[34], the effective Hamiltonians H'_{D} and H'_{A} were obtained by applying an external electric field directed along the line connecting donor and acceptor atoms. This field breaks the symmetry of the system and leads to localization of the electron on donor or acceptor sites. The field in this case should be sufficiently strong to decouple states D and A and to prevent their mixing, but not too strong to prevent the change of the potential barrier separating the donor and acceptor wells. Specifically, the condition can be formulated as follows

$$|T_{\mathrm{DA}}| \ll e\epsilon L_{\mathrm{DA}} \ll \min|E_0 - E_i| \tag{3.9}$$

where e is the electron charge, ϵ is the intensity of the applied field, and L_{DA} is the distance between donor and acceptor atoms (or complexes). The right-hand side of this inequality is the minimum distance between tunneling energy and excited states on the bridge. Since the tunneling matrix elements of our interest are of the order of hundreds of inverse centimeters or less and the barriers are of the order of several electronvolts and in any case $|T_{\mathrm{DA}}| \ll \min|E_0 - E_i|$, this condition can be easily satisfied. If the condition 3.9 is satisfied, the calculated properties of the system, such as tunneling matrix element T_{DA} and others, should be independent of the particular value of ϵ.

Once the approximate donor and acceptor wave functions are found, the calculation usually proceeds with the evaluation of the tunneling matrix element by eq 2.7, where instead of exact ψ_{D} and ψ_{A} their approximations ψ'_{D} and ψ'_{A} are used.

We notice one seemingly striking problem with this method of evaluation of T_{DA}. Since ψ'_{D} is much different from the exact ψ_{D} in the region of the acceptor, and ψ'_{A} much different from the exact ψ_{A} in the region of the donor, their product is ill-defined in most of the regions of the space. Since T_{DA} is defined by the integral of the product of ψ'_{D} and ψ'_{A}, one might ask how is it possible then to get an accurate value of T_{DA} without knowing exact functions ψ_{D} and ψ_{A}?

Our reformulation of the tunneling problem in terms of the currents helps to explain the puzzle. Equation 2.17 for matrix element in terms of the tunneling current J is equivalent to the conventional formula; however, since it involves only surface integral, instead of volume integral as in eq 2.7, it shows that there are significant cancellations in the volume integral and the net result for T_{DA} depends only on the value of the donor and acceptor wave functions and their derivatives on the surface separating donor and acceptor in the region of the bridge.

The nature of these cancellations is already obvious from eq 2.7. In this equation the volume integral in the region of the acceptor site is zero, since ψ'_{A} satisfies the Schrödinger equation

$$H\psi'_{\mathrm{A}}(x) = E_0\psi'_{\mathrm{A}}, \quad x \in \Omega_{\mathrm{A}} \tag{3.10}$$

In the rest of the space, the integrand in the volume integral turns out to be a div of some field (current) and therefore, using Gauss' theorem, can be written as a surface integral. The cancellations are due to the fact the integrand in the volume integral has a form of a divergence of some field.

Thus we arrive at a surprising conclusion that the wave functions that are apparently incorrect in most of the regions of space can give, nevertheless, an accurate value for the tunneling matrix element. The reason is that the tunneling matrix element is determined only by the values of the wave functions in the narrow region under the barrier, where our procedure for evaluation of *both* functions ψ'_{D} and ψ'_{A} is sufficiently accurate.

In our calculations a weak electric field ϵ was applied to the system; two opposite directions of the applied field resulted in two ground states that are localized on the two atoms on the opposite sides of the molecules and have exponential tails extending into the bridge. These two states correspond to donor and acceptor. This procedure results in molecular orbitals of D and A states, which are then biorthogonalized. After that current density was calculated as described in the previous section. The wave functions were determined using GAUSSIAN-94 electronic structure program.[48]

4. Numerical Examples of Current Density Calculations

In this section we present results of calculations of tunneling currents in several model resonant charge exchange systems $\mathrm{M}-(\mathrm{B}_1...\mathrm{B}_n)-\mathrm{M}^+$. Each of the systems consists of an atom M exchanging an electron with its ion M^+, and M and M^+ are separated by a linear array of additional atoms $\mathrm{B}_1...\mathrm{B}_n$ (or ions) located on the straight line connecting M and M^+. The atoms

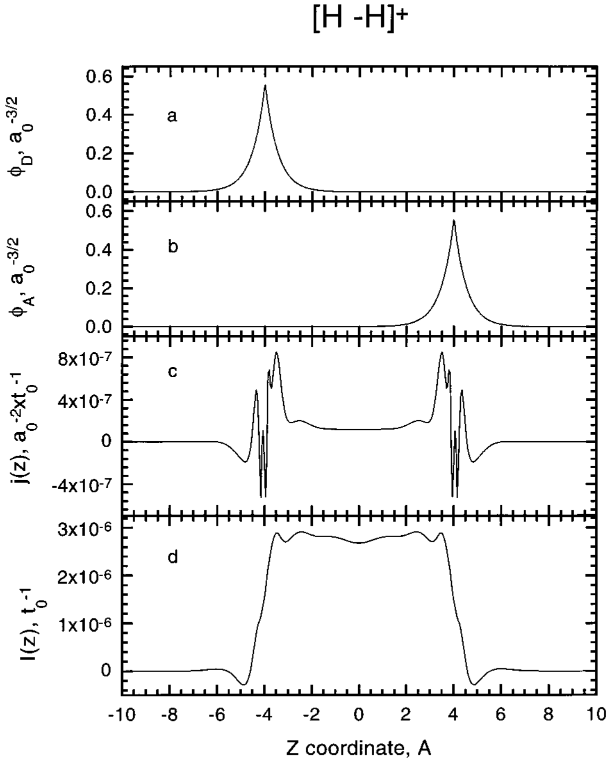

Figure 1. (a, b) Donor and acceptor wave functions (along the internuclear axis) in the H_2^+ system. The states were localized by applying an electric field along the symmetry axis of the molecule. Donor and acceptor are separated by 8 Å. An optimized basis set was used (see text). (c) Current density for H_2^+ along the internuclear axis. (d) Total flux as defined by eq 4.1.

between donor M and acceptor M^+ play the role of the bridge. Our goal here is to examine tunneling currents in such systems using the method discussed in the previous sections and to answer few principal questions, such as the following: (1) how does a resonant exchange between many-electron atoms/ions occurs through space; (2) what exactly happens when an electron tunnels through an atom of the bridge or a series of the atoms in the bridge, and (3) how accurately can one describe the tails of the atomic wave functions that one needs for the description of tunneling currents with the methods of quantum chemistry, i.e., using standard Gaussian basis functions.

4.1. Tunneling through Space. We begin the discussion of the numerical results from the simplest case of a system of two protons exchanging an electron. (For H_2^+ system, there exist an analytical solution, and the accuracy of numerical calculations, as well as the quality of some approximations, can be easily evaluated.) The distance between the protons was chosen to be 8 Å. The main challenge in this system was to optimize the Gaussian basis to cover such unusually large distances.

Figure 1 shows donor and acceptor wave functions, $\psi'_{D,A}$, current density, $J_z(z)$, and the total flux, $I(z)$, along the *z*-axis connecting the two ions of H_2^+ system. The total flux, or total current, is the integral of the current density J_z over the plane perpendicular to the *z*-axis and crossing it at point *z*.

$$I(z) = \int_{S_z} d\vec{s}\ \vec{J}(\vec{x}) = \int\int dx dy\, J_z(x, y, z) \tag{4.1}$$

The basis set was optimized (by minimizing the energy of donor and acceptor states) and contained eight s-, three p-, and one d-Gaussian shells. The largest exponent was approximately 2.5 × 10^2 and the smallest one 0.05. Thus, in principle, the two basis sets together could cover the whole range between donor and acceptor. One should remember, however, that the donor and acceptor wave functions that we are using, ψ'_{DA}, give poor approximation for the exact functions in the vicinity of the partner's well, as discussed in the previous section. In a separate calculation, by directly evaluating symmetric ψ_a and antisymmetric ψ_b states, we have checked that indeed this is the case.

The behaviors of the wave functions in the whole range between donor and acceptor are important since the current at a given point in space is determined by the product of one function and the derivative of the other at that point. The features of the tails of the wave functions are too small to be noticeable in Figures 1a,b.

Figure 1c shows seemingly irregular behavior of the current in the vicinity of each of the nuclei. The irregularities are due to different Gaussians with large exponents covering the very core region of the nuclei. It should be recalled that the current in this region is not well-defined, because of the problem with the tails of the wave functions (in the very vicinity of the other well) discussed above.

On the other hand, in the region *between* the two protons, i.e., under the barrier, the tails of our wave functions, as well as their multi-gaussian representation, is of satisfactory quality. The evidence for this comes from Figure 1d, which shows the behavior of the total current as a function of the *z*-coordinate.

The key test of the quality of our results for current in the region of the barrier is based on our eq 2.16, which seems to be of fundamental importance. It states that the divergence of the tunneling current density at a given point is proportional to the differential density of donor and acceptor states at that point, with the tunneling matrix element T_{DA} being the proportionality coefficient. The right- and the left-hand sides of this equation can be calculated for arbitrary functions ψ_D and ψ_A; however, it is only when these functions are exact donor and acceptor states, in the sense discussed in the previous section, that the right- and the left-hand sides will coincide at all points in space.

We notice that one side of this equation containing differential density is everywhere well-defined, even with our approximate functions, while the other is not. The reason for that is that in the very vicinity of the either of the nuclei, where the problem with the tails of the wave function arises, the large and well-defined density, say ρ^D, is so much greater than the small and ill-defined counterpart, ρ^A, that the value of the difference, $\rho^D - \rho^A$, is completely defined only by the large and well-defined term (order of unity). On the other hand, the side of the equation containing currents is much more sensitive to the quality of the wave functions. The small parameter T_{DA} determines the magnitude of the numerical values that are compared in the right- and the left-hand sides of the equation.

Instead of checking balance of the right- and the left-hand sides of eq 2.16 everywhere in space, we examine this equation in its integral form. If we integrate eq 2.16 over the volume of half-space limited from the -∞ side by a plane S_z perpendicular to the *z*-axis

$$I(z) = -\frac{T_{DA}}{\hbar}\int_{-\infty}^{z} dv(\rho^D(\vec{x}) - \rho^A(\vec{x})) \tag{4.2}$$

where $\rho^A(\vec{x})$ and $\rho^D(\vec{x})$ are electron densities in the A and D states and $I(z)$ is the total current though the surface defined by eq 4.1. We assume that the donor is placed at negative *z* (-4 Å in Figure 1) and the acceptor is at positive *z* along the *z*-axis.

The qualitative analysis of eq 4.2 is straightforward. In the vicinity of the donor site, the donor density always dominates

TABLE 1: Comparison of T_{DA} Calculated with the Tunneling Flux Method and as a Direct One-Half Splitting of the Symmetric and Antisymmetric States

molecule	T_{DA} (cm^{-1})	$\Delta E/2$ (cm^{-1})
$[H-H]^+$	0.59	0.67
$[Li-Li]^+$	359.0	447.0
$[Na-Na]^+$	502.0	629.0

over that of the acceptor. Since density is everywhere positive, the integral in the above equation, as a function of coordinate z, starts from zero at $-\infty$ and reaches its maximum value $-T_{DA}$ in the region somewhere between donor and acceptor. Further shift of the plane S_z toward the acceptor will lead to the opposite behavior, and the integral will become again zero as $z \rightarrow \infty$. For symmetric systems, such as ours, the function $I(z)$ is even.

In Figure 1d the total current $I(z)$ calculated by eq 4.1 is shown. It is seen that the qualitative behavior of $I(z)$ indeed corresponds to that described above. The small deviations from the monotonous behavior that are seen in the figure are due to the deviation of our wave functions ψ'_D and ψ'_A from their exact values. As we remarked earlier, there are two sources of errors in the wave functions. First is that our effective Hamiltonians, H'_D and H'_A, employed in calculation of ψ'_D and ψ'_A are incorrect in the vicinity of the second nucleus. And the second is that our Gaussian basis is not capable of capturing all details of exponential tails of the wave functions in the region of the barrier. Fluctuations in the region between donor and acceptor are due to this effect. These fluctuations, however, are relatively small—in the range of 10−20%.

Another test of the quality of our calculations is to compare the saturated value of the total current with its theoretical value, $-T_{DA}$. For this end for H_2^+ and other simple models of this paper, the matrix element was determined directly as half of the splitting between energies of antisymmetric and symmetric states of the unperturbed systems (i.e., without an electric field). One state of these two is the ground state, and the other is the first excited state. The two states were determined in a SCF procedure in a one-determinant approximation with the same basis set used for current calculations. We find that the two matrix elements, one from the direct calculation, another from the saturated value of the current in the barrier region, coincide within 10−20% or better (see below). Results for H_2^+ and some other systems are shown in Table 1 and further discussed below.

Given the approximate nature of the wave functions, the agreement within 10−20% of these two methods is rather surprising. Because of the sensitivity of the tunneling matrix elements to exponentially small tails of the wave functions, neither method can be regarded a priori as reliable. Comparison of two completely different methods of calculations sheds some light on the accuracy of such calculations.

In Figure 2 results of similar calculations are shown for the Na_2^+ system. It is seen that the many-electron nature does not add anything qualitatively new. We have done also similar calculations on Li_2^+. The strongest contribution to tunneling current in these systems was found to be due to the outermost electron moving in the effective field of nuclei and that of other electrons in the system. In Figure 3 the distribution of the tunneling current density for the Na_2^+ system is shown.

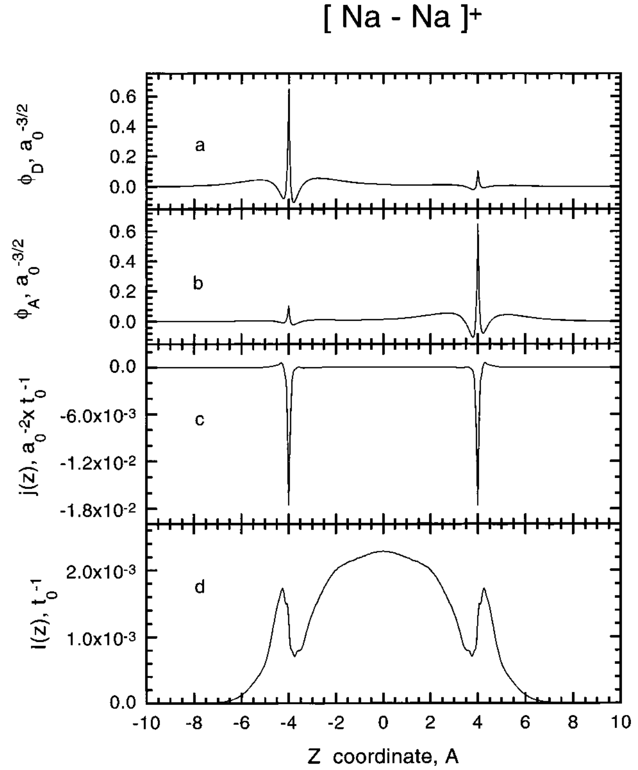

Figure 2. (a, b) Donor and acceptor wave functions (along the internuclear axis) in the Na_2^+ system. Details are the same as in Figure 1. (c) Current density for Na_2^+ along the symmetry axis of the molecule. (d) Total flux as defined by eq 4.1.

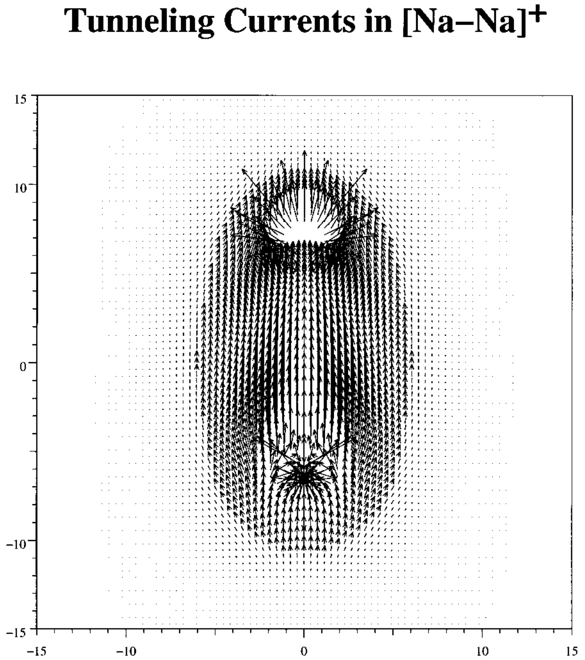

Figure 3. Distribution of tunneling current density in Na_2^+ calculated using the standard 6-311G basis set. All units are in bohr (a_0). Donor and acceptor are separated by 7 Å.

4.2. Tunneling through a Bridge. How Does an Electron Tunnel through an Atom? Here we discuss results of our calculation of the $H-(He)_n-H^+$ system, in which two protons exchange an electron via a string of helium atoms. Two basis sets used in the calculations were 6-311G and 6-311++G(2df,2p). The extended basis set gives essentially the same results as 6-311 but with better resolution of small details of the currents.

We found that the transition between highest occupied orbitals carries most important information about the tunneling process. This is an indication that the one-electron description of the tunneling process is in principle possible, provided the interac-

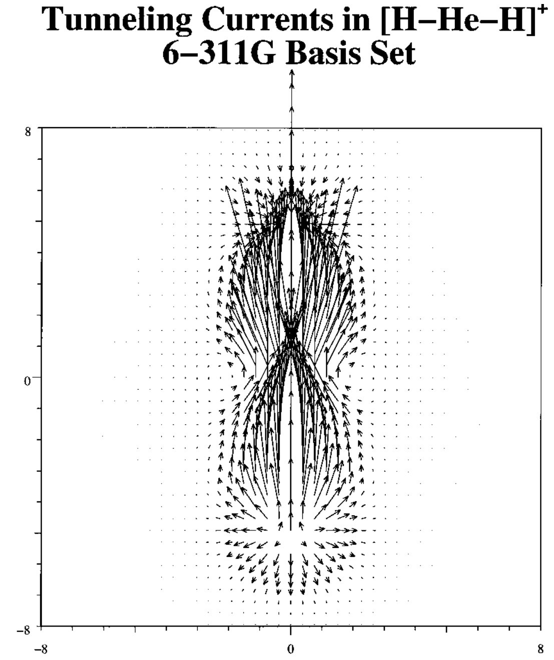

Figure 4. Tunneling currents in a system $[H-(He)_n-H]^+$ with one bridge atom, $n = 1$. Donor and acceptor are separated from the bridge atom by 2.5 Å.

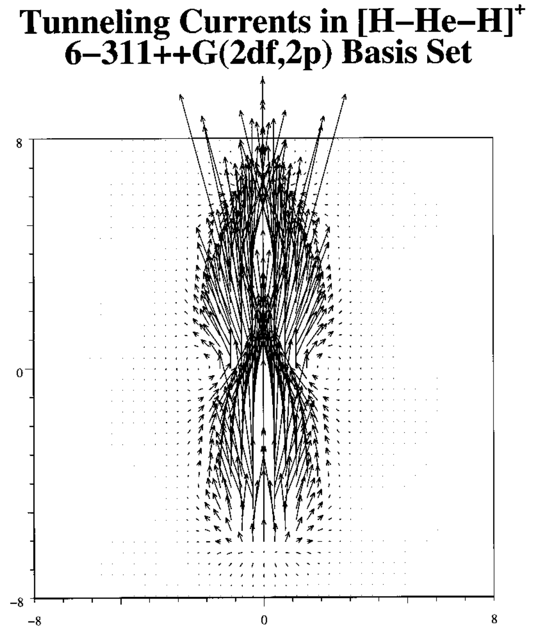

Figure 5. Same as in Figure 4, but calculated using a 6-311++G-(2pd,2f) basis set.

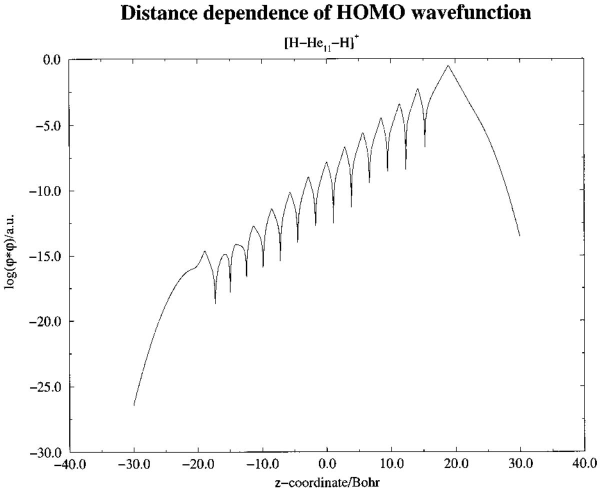

Figure 6. Distance dependence of the donor (acceptor) wave function in the $[H-(He)_n-H]^+$ system, $n = 11$, along the symmetry axis of the molecule. Donor and acceptor (H atoms) are separated from the bridge by 2.5 Å. He atoms within the bridge are separated by 1.5 Å. The total separation of donor from acceptor atoms is exactly 20 Å. The ln of the square of the wave function decays linearly with distance with a decay constant of 0.9 a_0^{-1}.

tion of "the tunneling electron" with other electrons (including the exchange interactions) are properly taken into account. The internal orbital currents reflect the polarization response to the tunneling charge. In the total current, the polarization component usually masks some important details of the current associated with the long-distance electron transfer. We therefore focus in the following discussion on the currents originating between the HOMO's of the donor and acceptor states. The biorthogonalization procedure was found to introduce only small changes of the molecular orbitals since the original orbitals taken from the output of the Gaussian calculation already have very small overlaps; i.e., these orbitals are already almost biorthogonal.

Figure 4 shows distribution of tunneling currents in a system with one bridge atom. The data allows one to gain insight into the nontrivial question of how exactly a tunneling electron penetrates a bridge atom. The results are counterintuitive. The expectation is that owing to the Pauli exclusion principle, the tunneling electron will try to avoid the repulsive core region of the bridge atom. However, we find that the very same repulsion results in antibonding mixing of the wave function of the tunneling electron and that of the core and, as a result, leads to a significant current directly through the center of the bridge atom. Figure 5 shows the same data as in Figure 4 but calculated with the extended basis set. Results, as seen, are essentially identical with those of a more primitive basis set.

The polarization currents in the system flow in the opposite direction to that of the tunneling electron. These currents are localized on the atoms of the bridge and are due to a "shift" of electron density on these atoms resulting from the long-range Coulombic interaction with the tunneling electron.

In Figure 6 the initial wave function of the tunneling electron is shown for a $H-(He)_n-H^+$ system with $n = 11$. A perfect exponential decay of the amplitude of the initial function on the bridge atoms with increasing distance is worth noticing. Such a perfect exponential dependence with distance obviously is a result of the homogeneous (and periodic) nature of the bridge. It is interesting that the boundary effects show up only at the very vicinity of the donor and acceptor atoms. The numerical values of the wave function were verified with two different basis sets.

Figure 7 shows the total flux through a dividing surface along the axis connecting donor and acceptor atoms in a representative system with $n = 9$. As was explained above in the text, the nonmonotonic behavior of this function is in part due to the deviation of the wave functions found in the variational procedure from those that are exact solutions of the Schrödinger equation. the most important part of the flux dependence shown in Figure 7 is roughly in the middle of the bridge. According to theory presented above, the saturated value of the flux in the region between donor and acceptor should coincide with the value of the tunneling matrix element, eq 2.17. In Figure 8 a comparison is shown of the matrix elements calculated with eq 2.17 with those directly evaluated by the splitting of the symmetric and antysymmetric states in the unperturbed system.

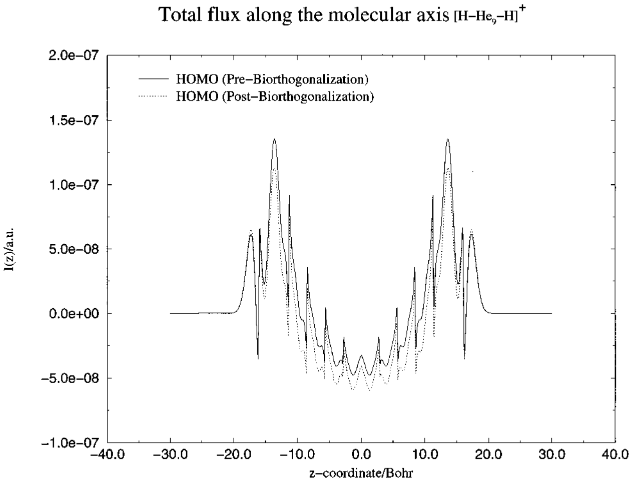

Figure 7. Total tunneling flux along the molecular symmetry axis, z, in the $[H-(He)_n-H]^+$ system. Here the system is composed of a nine-atom helium bridge separated by 1.5 Å and coupled to donor and acceptor H atoms at a distance of 2.5 Å. The flux was calculated using HOMO before (solid line) and after (dashed line) the biorthogonalization.

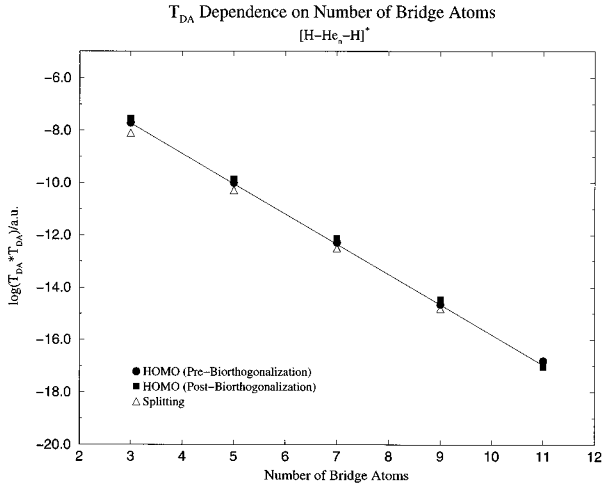

Figure 8. Distance dependence of electronic coupling T_{DA} in $[H-(He)_n-H]^+$ system with $n = 3-11$. Two filled symbols correspond to calculations using the theory of the present paper. Squares and circles correspond to results obtained with and without biorthogonalization of molecular orbitals of donor and acceptor states. The open triangles correspond to calculated electronic coupling using the direct method of evaluating the splitting between symmetric and antisymmetric states. The distance dependence of the coupling is exponential, $T_{DA} = A\,\exp(-\beta \cdot R/2)$. The attenuation factor of the coupling $\beta = 0.9\ a_0^{-1}$, which is the same as that of the wave function, Figure 6.

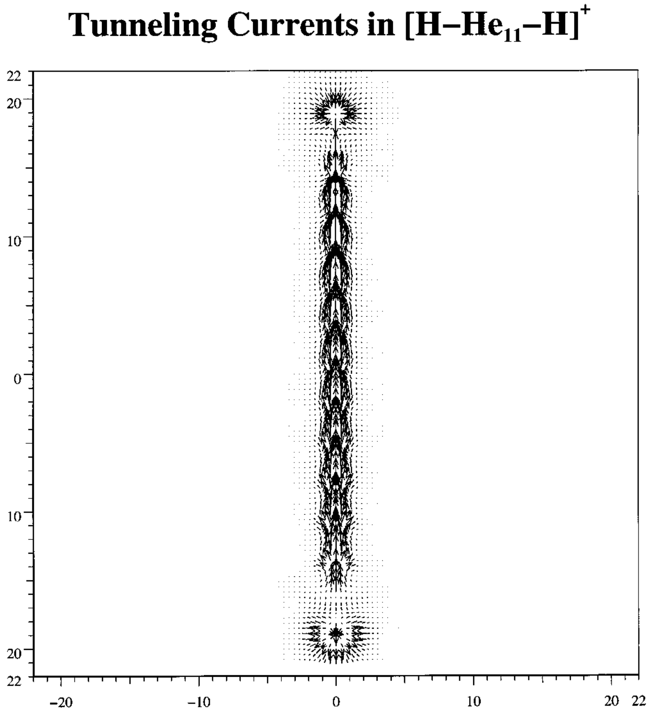

Figure 9. Tunneling currents for a system with an 11-atom bridge. Donor and acceptor (H atoms) are separated from the bridge by 2.5 Å. He atoms within the bridge are separated by 1.5 Å. Here the donor is at the bottom of the figure. All length units are in bohr (a_0). The extended 6-311 basis set was used.

As is seen from the figure, there is a perfect agreement between calculated values of the matrix elements with two totally different methods. For a system of 11 bridge atoms, the splitting of symmetric and antisymmetric states was so small that it was not possible to determine it within the numerical accuracy of the energy calculations. Yet the method based on eq 2.17 still was able to yield the magnitude of the tunneling matrix element, which apparently is in line with the other calculations shown in this figure. The perfect exponential dependence of the tunneling coupling in these linear systems is in agreement with the expected behavior.

It is worthy to mention that the tunneling matrix element in $H-(He)_n-H^+$ systems is positive. That is, the ground state HOMO is antisymmetric. It appears at a first glance that the wave function antisymmetry means that the He atoms would try to block the tunneling electron, and yet it is clearly seen from the results of the calculations that a string of 11 He atoms can propagate the tunneling electron over distances as large as 20 Å. This remarkable phenomenon is most clearly presented in Figure 9 where almost a constant stream of the tunneling current from donor to acceptor through the bridge of 11 atoms is clearly seen. Such tunneling streams obviously exist in electron-transfer proteins and make what is called the "tunneling pathways".[17]

5. Conclusion

We have presented the first full ab initio implementation of the method of tunneling currents for the description of long-distance electron-transfer reactions. Results were obtained for $[H-(He)_n-H]^+$ model systems, with $n = 0-11$. These and other systems that we have examined allow us to draw the following conclusions. The method is capable of providing new insights into the process of long-distance tunneling with its detailed, essentially subatomic, description of the tunneling process. A satisfactory description of the through-space tunneling currents over distances up to 8 Å can be achieved with specially optimized basis sets. In calculations of through-bond interatomic tunneling currents, when the distances between atoms is in the range of 1.5−2.5 Å, standard basis sets can be used. The tunneling currents consist of the contribution of the donor and acceptor highest occupied molecular orbitals and the polarization currents originating from the other orbitals in the system. An excellent agreement of the method of tunneling currents with the results of direct evaluation of the transfer matrix element is obtained when the currents of the HOMO's are used in the calculation. The biorthogonalization of the orbitals of donor and acceptor states does not change significantly results of the calculations.

The method described in this paper provides a detailed description of electron delocalization dynamics and as such can be a useful tool in the analysis of long-distance electron tunneling in proteins or in other organic materials with complex structural organization. In particular, the quality of the previous one-electron theories will be possible to test now against ab initio calculations of the tunneling pathways. Also, the effect of dynamics[16] and disorder[20] of protein matrix on long-distance tunneling in biological systems will now be possible to address at a more accurate level of calculations.

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