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Quantum Chemical Approach to Electron Transfer in Molecular Systems

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A theoretical treatment of electron transfer in and between molecules is presented. The nuclei are assumed to move classically. A time-dependent electron probability density is calculated using general equations given by Nikitin. Variational methods of different kinds may be employed in these equations. In the present paper some examples are studied at the extended Hückel level for the systems H_2–H_2^+, H_2–O^{2-}–H_2^+, H_2–S^{2-}–H_2^+ and H_2–H_2–H_2^+.

Key words: Electron transfer – theoretical – time dependent – Nikitin equations – extended Hückel – adiabatic – nonadiabatic – molecular orbitals.

1. Introduction

Electron transfer is a commonly occurring phenomenon of great interest in as diverse fields as atomic physics including astrophysics, semiconductor physics, organic and inorganic chemistry and biochemistry [1]. In condensed systems electron transfer is due to photoexcitations or thermal motions of the nuclei. In the theory of R. A. Marcus a rate constant is calculated assuming classical motion of the nuclei [2]. The barrier for thermal excitation may be related to the optical excitation energy for corresponding light induced electron transfer (Fig. 1) [3]. In more recent theoretical developments the nuclear motions are treated quantum mechanically [4–7]. An interesting comparison between the quantum mechanical and classical treatment of the nuclear problem was published recently [8, 9]. With a few notable exceptions [10–14] the medium between the electron exchanging centers has been considered without any regard to the electronic properties of the molecules it consists of. This problem is of great importance since the electronic structure of the medium decides whether the exchange

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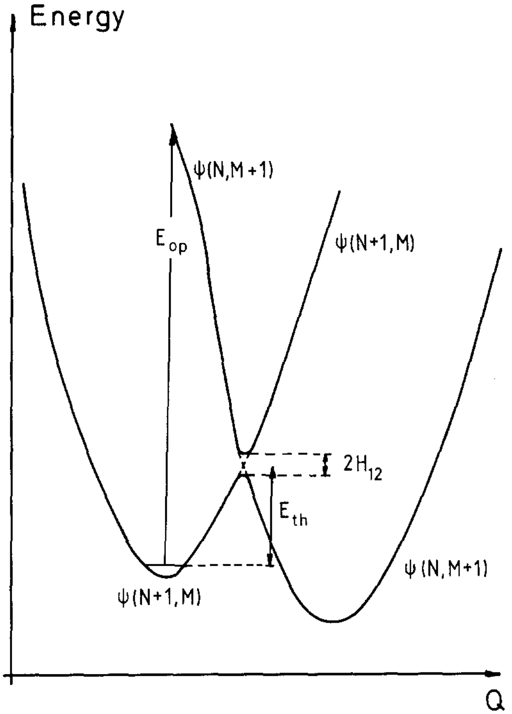

Fig. 1. Model for electron transfer in condensed systems [2, 3]

reaction is adiabatic or approaches the nonadiabatic limit where no electron transfer takes place. In the present paper this problem will be studied by quantum chemical methods.

In quantum chemistry one usually deals with the calculation of the energies and wave functions of the ground state and a few excited states for one or a few nuclear geometries. It is easy to find examples of "avoided crossings" of energy surfaces. To study the flow of electron probability density at such crossings it is necessary to use a theory which allows for nonadiabatic transitions between the energy surfaces. Landau [15] and Zener [16] have given an equation to calculate the probability for jump in the simplest possible case when two states with energies $H_{11}(t)$ and $H_{22}(t)$ interact and have the time independent interaction matrix element H_{12}. The wave functions u_1 and u_2 for each system when isolated, may be considered as orthogonal basis functions which leads to the secular problem:

$$\begin{vmatrix} H_{11}-\varepsilon & H_{12} \\ H_{12} & H_{22}-\varepsilon \end{vmatrix} = 0. \tag{1}$$

The time dependence in u_1 and u_2 is ignored. For a given time the solution of Eq. (14) may be written as:

$$\begin{aligned} E_1 &= H_{22} + H_{12} \cot \eta \\ E_2 &= H_{11} - H_{12} \cot \eta \end{aligned} \tag{2}$$

where

$$\mathrm{tg}\, 2\eta = \frac{2H_{12}}{H_{11}-H_{22}} \tag{3}$$

(using the branch $\pi/2 < 2\eta < 0$ when $H_{22} > H_{11}$ and $\pi < 2\eta < \pi/2$ when $H_{11} > H_{22}$). The corresponding wave functions are:

$$\begin{aligned} \psi_1 &= \cos\eta\, u_1 + \sin\eta\, u_2 \\ \psi_2 &= \sin\eta\, u_1 - \cos\eta\, u_2. \end{aligned} \tag{4}$$

The smallest energy difference is obtained for $\eta = \pi/4$:

$$H_{11} = H_{22}; \qquad E_2 - E_1 = -2H_{12}. \tag{5}$$

Zener obtained the time dependent solution of Eq. (2) (under certain conditions) [6], whereas Landau treated the problem by perturbation theory [15]. The probability for jump from the lower surface to the upper one is:

$$P = \exp\left[-2\pi(2H_{12})^2 \Big/ \frac{\partial}{\partial t}(H_{11}-H_{22})\right]. \tag{6}$$

From Eq. (6) follows that the probability for jump tends to unity as H_{12} tends to zero (nonadiabatic behaviour).

Although the Landau–Zener relation has proven to be very useful there are a number of objections to general applications of it. In a variational calculation it may not be possible to write the secular problem even approximately as in Eq. (1) with a well-defined matrix element H_{12}. If, alternatively, H_{12} is defined as half the gap between the energy surfaces, it may not be possible to define H_{11} and H_{22} strictly. In applications of Eq. (6) H_{11} and H_{22} are obtained as asymptotes of the energy surfaces. This may be possible in a collision between two particles which are at infinite separation at $t = -\infty$ and $t = \infty$, but less appropriate in condensed systems where the nuclei are confined to a certain region and where the energy surfaces may cross repeatedly along the nuclear

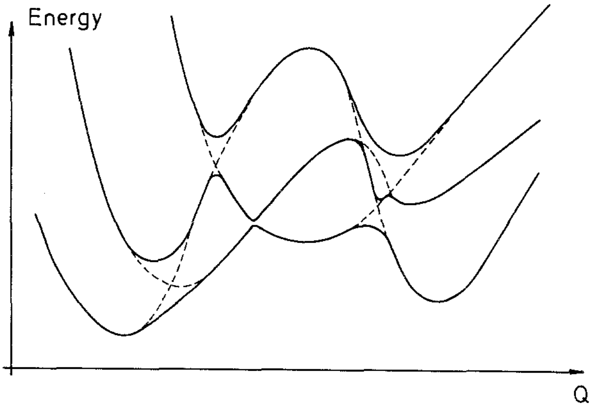

Fig. 2. Crossing energy surfaces illustrating the difficulties in the Landau–Zener model

trajectory (Fig. 2). Some crossings may involve more than two states. Finally the physical siutation may require more than two stationary states to form a "prepared state", i.e. to describe a known charge distribution at a given time. It is thus necessary to extend the theory beyond the Landau–Zener approach.

In this paper a time dependent approach of Nikitin [17] will be developed to obtain a time dependent electron probability density. Only wave functions and energies need to be calculated in a number of points along a classical nuclear trajectory. In each point the Born–Oppenheimer approximation is assumed. The approach is therefore well suited for any quantum chemical calculational method.

The ultimate purpose with the method to be presented here is to get a better understanding of electron transfer in large systems where a nonadiabatic behaviour may be important, as for instance the cytochromes of the respiratory chain. To that end it seems more important to get a qualitative understanding of electron transfer systems by simple quantum chemical methods than to obtain detailed data for a small system by advanced methods. In this paper the extended Hückel method [18] will be used. Detailed applications with more sophisticated methods will be postponed to a later stage.

2. Time Independent Hamiltonian

Let us first study the time dependence of the electronic density in the case of a time independent hamiltonian, i.e. in the limit when the velocities of the nuclei tend to zero. We assume that a single molecule or a well defined part of a macromolecule at time $t=0$ is described by a wave function $\psi(1,2,\ldots,N;0)$. ψ may be expanded in terms of eigenfunctions of the Hamiltonian H of the system:

$$\psi(1,2,\ldots,N;0)=\sum_l a_l\phi_l(1,2,\ldots,N) \tag{7}$$

where

$$H\phi_l=E_l\phi_l{}^1 \tag{8}$$

and

$$a_l=\langle\phi_l|\psi\rangle. \tag{9}$$

Assuming that H is time independent the time evolution is given by:

$$\psi=\sum_l a_l\phi_l\exp(-iE_lt). \tag{10}$$

Atomic units are used throughout: $E_a=4.36\times10^{-18}$ J; $t_a=\hbar E_a^{-1}=2.419\times10^{-17}$ sec. The wave function ψ satisfies the time dependent Schrödinger

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[1] Since variationally calculated eigenfunctions and eigenvalues do not strictly satisfy Eq. (8) we may have to redefine H as an approximate "variational" operator $H'=\sum E_l|\phi_l\rangle\langle\phi_l|$ which satisfies Eq. (8).

equation:

$$i\frac{\partial\psi}{\partial t} = H\psi = \sum_l a_l E_l \phi_l \exp(-iE_l t). \tag{11}$$

Introducing the spin independent transition densities

$$\rho_{kl}(\boldsymbol{r}_1) = N\int \phi_k(1, 2, \ldots, N)\bar{\phi}_l(1, 2, \ldots, N)\, ds_1\, d_2 \ldots dN \tag{12}$$

the electronic density of the system, normalized to N electrons, will be:

$$\begin{aligned}\rho(\boldsymbol{r}, t) &= N\int \psi\psi^*\, ds_1\, d2 \ldots dN \\ &= \sum_{k,l} a_k a_l^* \rho_{kl} \exp[-i(E_k - E_l)t].\end{aligned} \tag{13}$$

In the usual case $\{a_j\}$ and $\{\rho_{jk}\}$ are real quantities and Eq. (13) may then be written:

$$\rho(\boldsymbol{r}, t) = \rho(\boldsymbol{r}, 0) - 4\sum_{k<l} a_k a_l \rho_{kl} \sin^2\left(\frac{E_k - E_l}{2} t\right) \tag{14}$$

Of course, if ψ happens to be an eigenfunction of H, i.e. only one a_k in Eq. (7) is different from zero, the density will be independent of time.

As an example we may choose H_2^+. The two $1s$ functions are denoted ϕ_A and ϕ_B. We assume that the electron occupies ϕ_A at time $t = 0$. Eq. (7) corresponds to:

$$\phi_A = \frac{1}{\sqrt{2}}\left(\frac{\phi_A + \phi_B}{\sqrt{2}}\right) + \frac{1}{\sqrt{2}}\left(\frac{\phi_A - \phi_B}{\sqrt{2}}\right) \tag{15}$$

and Eq. (14) to:

$$\rho(\boldsymbol{r}, t) = \phi_A^2(\boldsymbol{r}) - [\phi_A^2(\boldsymbol{r}) - \phi_B^2(\boldsymbol{r})] \sin^2\left(\frac{E_1 - E_2}{2} t\right). \tag{16}$$

The electron will oscillate between A and B with the frequency $\nu = (E_2 - E_1)/2\pi$. At large distance R, the frequency rapidly tends to zero since [19]

$$E_2 - E_1 = \left(\frac{4}{3}R - \frac{2}{R}\right)e^{-R}. \tag{17}$$

At 10 Å, $\nu = 10^9\ \text{sec}^{-1}$; at 20 Å, $\nu = 13\ \text{sec}^{-1}$, for example.

Multiplying Eq. (11) by the complex conjugate of ψ [Eq. (10)] and integrating we obtain an equation for the energy of the system:

$$E = \langle\psi|H|\psi\rangle = \sum_l |a_l|^2 E_l \geq E_0. \tag{18}$$

$E - E_0$ is the energy required to prepare the system in the state ψ. Hence localization of an electron to a certain atom or molecular group requires energy. In biological electron transfers a "chemical mechanism" whereby the electrons travel from one group to the other, is sometimes discussed. This model has definite limitations since the energy for localization often turns out to be large. Below we will discuss molecular "bridges" as mediators of electrons. The bridges are different in this respect since the transferring electron has a small probability at all times to be found on the bridge.

In atom-ion scattering the charges are localized at time $t=-\infty$. The case of $H+H^+$ is rather special since the two sub-systems are identical and therefore resonate when brought together. It is perhaps instructive to study the case of different systems, still with no energy surface crossing. To localize one electron on A, Eq. (4) requires $a_1=\cos\eta$ and $a_2=\sin\eta$. Inserting in Eq. (14) we obtain:

$$\rho(\boldsymbol{r},t)=\rho_A-4\cos\eta\sin\eta\,[\cos\eta\sin\eta\rho_A-\cos\eta\sin\eta\rho_B]\sin^2\left(\frac{E_1-E_2}{2}t\right)$$

$$=\rho_A\left[1-\sin^2 2\eta\sin^2\left(\frac{E_1-E_2}{2}t\right)\right]+\rho_B\sin^2 2\eta\sin^2\left(\frac{E_1-E_2}{2}t\right). \quad (19)$$

Since E_1-E_2 and $H_{11}-H_{22}$ are large the oscillations will be rapid. η is small and hence the probability on ρ_B will be $\sim 2\sin^2\eta$ which is twice as large as the value in the ground state, but still very small. From Eq. (4) follows that $H_{22}-H_{11}$ has to be of the order H_{12} in order to obtain a charge exchange of any magnitude. The system thus has to be brought to, or close to, the avoided crossing region of two or more energy surfaces. The magnitude of H_{12} is critical in two respects. It determines the size of the region where electron exchange is possible and at the same time the frequency of the charge oscillations. This "explains" the square dependence of H_{12} in the Landau–Zener equation. The limit of small H_{12} will be further studied in the next section.

3. Time Dependent Nuclear Motion

We will follow the semi-classical approach of Nikitin where the nuclei are assumed to follow a classical trajectory $\boldsymbol{R}(t)$ [17]. The electronic wave functions, $\{\phi_l\}$, are calculated in a sufficiently dense grid along this trajectory. Eqs. (8) and (9) are satisfied but $\{\phi_l\}$ and a_l are now time dependent. Instead of Eq. (10) we will write, following Nikitin:

$$\psi=\sum_l a_l(t)\phi_l(1,\ldots,N;t)\exp\left[-i\int_0^t E_l\,d\tau\right]. \quad (20)$$

We have:

$$H\psi=\sum_l a_lE_l\phi_l\exp\left[-i\int_0^t E_l\,d\tau\right]. \quad (21)$$

Multiplying Eq. (21) by the complex conjugate of ψ and integrating, Eq. (18) is again obtained. Inserting Eq. (20) in

$$i\frac{\partial\psi}{\partial t}=H\psi, \quad (22)$$

multiplying with the complex conjugate of ϕ_l and integrating one obtains the following system of equations:

$$\frac{da_l}{dt}=\sum_m a_m\left\langle\phi_l \,\middle|\, \frac{\partial\phi_m}{\partial t}\right\rangle \exp\left[-i\int_0^t (E_m-E_l)\,d\tau\right]. \tag{23}$$

If we define a velocity v along the trajectory:

$$v=\left|\frac{\partial\vec{\boldsymbol{R}}}{\partial t}\right|=\frac{\partial Q}{\partial t} \tag{24}$$

we arrive at the equation system

$$\frac{da_l}{dQ}=\sum_m a_m\left\langle\phi_l\middle|\frac{\partial}{\partial Q}\middle|\phi_m\right\rangle \exp\left[-i\int_0^Q (E_m-E_l)\frac{dQ'}{v}\right] \tag{25}$$

(Q and Q' are coordinates along the trajectory). The matrix elements of $\partial/\partial Q$ are obtained by calculating ϕ_m in two close points, i and j, and use:

$$\left\langle\phi_l\middle|\frac{\partial}{\partial Q}\middle|\phi_m\right\rangle=\frac{1}{\Delta Q}[\langle\phi_l^{(i)}|\phi_m^{(i)}\rangle-\langle\phi_l^{(i)}|\phi_m^{(j)}\rangle]. \tag{26}$$

The calculation of the matrix elements of $\partial/\partial Q$ is the time consuming part at least in the case of accurate wave functions of configuration interaction type. Interpolation functions may be used to describe the Q-variation of the matrix elements $\langle\phi_l|\partial/\partial Q|\phi_m\rangle$ [20].

After $\{da_l/dt\}$ have been obtained at $t=t_0$ either directly from Eq. (23) or via Eq. (25) using

$$\frac{da_l}{dt}=\frac{da_l}{dQ}\cdot\frac{dQ}{dt} \tag{27}$$

a new a_l for $t=t_1$ is obtained as

$$a_l^{(t_1)}=a_l^{(t_0)}+\left(\frac{da_l}{dt}\right)_{t0}\Delta t. \tag{28}$$

Subsequently the electronic density at $t=t_1$ is obtained as in Eq. (13) using the integral form in the exponential as in Eq. (20).

Non-zero matrix elements of $\partial/\partial t$ lead to non-adiabatic behaviour of various degrees. Using the wave function given in Eq. (4) and neglecting the weak time-dependence of the basis functions we obtain:

$$\left\langle\psi_2\middle|\frac{\partial}{\partial t}\middle|\psi_1\right\rangle=\frac{dy}{dt}\cdot\frac{d\eta}{dy}\cdot\left\langle\psi_2\middle|\frac{\partial}{\partial\eta}\middle|\psi_1\right\rangle=-\frac{\partial y}{\partial t}\cdot\frac{\partial\eta}{\partial y}$$

where

$$y=H_{11}-H_{22}. \tag{29}$$

Since

$$\frac{\partial \eta}{\partial y} = \frac{-H_{12}}{(2H_{12})^2 + y^2}$$

the matrix elements may be written as:

$$\left\langle \psi_2 \middle| \frac{\partial}{\partial t} \middle| \psi_1 \right\rangle = \frac{d(H_{11} - H_{22})/dt}{4H_{12}} \cdot \frac{1}{1 + \left(\frac{H_{11} - H_{22}}{2H_{12}}\right)^2}. \tag{30}$$

Comparison with the Landau–Zener equation, Eq. (6), shows that the matrix elements of $\partial/\partial t$ very appropriately may be called non-adiabatic coupling terms [17]. The width of the coupling region is $H_{11} - H_{22} = 2H_{12}$.

When $|H_{11} - H_{22}| \gg H_{12}$ the off-diagonal matrix elements of $\partial/\partial t$ are close to zero and the electron transfer almost adiabatic. The oscillations may be rapid but the amplitudes and the frequencies of the oscillations are slowly varying [cf. Eq. (19)]. In practical terms this means that a sparse integration mesh can be used. For small velocities the wave length of the oscillations may be smaller than the mesh which does not lead to any serious consequences. The adiabatic density fluctuations cannot and need not be followed in detail. They will be correct in some average sense.

4. Formal Aspects Normalization

Using finite differences Eq. (3) may be written in the form:

$$\begin{aligned} \boldsymbol{a}(t_1) &= \boldsymbol{a}(t_0) + d\boldsymbol{a}(t_0) \\ &= \begin{pmatrix} \exp\left(i \int_{t_0}^{t_1} E_1\, dt\right) & 0 & \cdots \\ 0 & \exp\left(i \int_{t_0}^{t_1} E_2\, dt\right) & \cdots \\ & & \ddots \end{pmatrix} \begin{pmatrix} \langle \phi_1^{(t_0)} | \phi_1^{(t_1)} \rangle \langle \phi_1^{(t_0)} | \phi_2^{(t_1)} \rangle & \cdots \\ \langle \phi_2^{(t_0)} | \phi_1^{(t_1)} \rangle \langle \phi_2^{(t_0)} | \phi_2^{(t_1)} \rangle & \cdots \\ \vdots & \end{pmatrix} \\ &\quad \times \begin{pmatrix} \exp\left(-i \int_{t_0}^{t_1} E_1\, dt\right) & \cdots \\ 0 & \cdots \\ \vdots & \ddots \end{pmatrix} \boldsymbol{a}(t_0) = \boldsymbol{S}_E^+(t_1 - t_0) \boldsymbol{S}_\phi(t_1, t_0) \boldsymbol{S}_E(t_1 - t_0) \boldsymbol{a}(t_0). \end{aligned} \tag{31}$$

Continuing in the interval (t_2, t_1) and using

$$\boldsymbol{S}_E(t_2 - t_0) \boldsymbol{S}_E^+(t_1 - t_0) = \boldsymbol{S}_E(t_2 - t_1) \tag{32}$$

we obtain:

$$\boldsymbol{a}(t_2) = \boldsymbol{S}_E^+(t_2 - t_0) \boldsymbol{S}_\phi(t_2, t_1) \boldsymbol{S}_E(t_2 - t_1) \boldsymbol{S}_\phi(t_1, t_0) \boldsymbol{S}_E(t_1 - t_0) \boldsymbol{a}(t_0) \tag{33}$$

and for any time $t_n > t_0$.

$$\begin{aligned} \boldsymbol{a}(t_n) &= \boldsymbol{S}_E^+(t_n - t_0) \boldsymbol{S}_\phi(t_n, t_{n-1}) \ldots \boldsymbol{S}_E(t_1 - t_0) \boldsymbol{a}(t_0) \\ &= \boldsymbol{S}_E^+(t_n - t_0) \boldsymbol{U}(t_n, t_0) \boldsymbol{a}(t_0). \end{aligned} \tag{34}$$

The operator U fulfills the relation:

$$\boldsymbol{U}(t, t_0) = \boldsymbol{U}(t, t')\boldsymbol{U}(t', t_0); \qquad t > t' > t_0. \tag{35}$$

Eq. (34) may also be expressed as:

$$\psi(t) = \boldsymbol{U}(t, t_0)\psi(t_0) \tag{36}$$

where ψ now is the coefficient matrix for the wave function ψ in the basis $\{\phi_l\}$. Provided that the operator $\boldsymbol{U}$ preserves normalization it is hence an evolution operator in the sense of Löwdin [21]. That ψ remains normalized follows from:

$$\boldsymbol{U}^{+}(t+dt, t)\boldsymbol{U}(t+dt, t) = \boldsymbol{S}_E^{+}(dt)\boldsymbol{S}_\Phi^{+}(t+dt, t)\boldsymbol{S}_\Phi(t+dt, t)\boldsymbol{S}_E(dt) = \mathbf{1} \tag{37}$$

where we have used

$$\boldsymbol{S}_\Phi^{+}\boldsymbol{S}_\Phi = \sum_j \langle \phi_i^{(t)} | \phi_j^{(t+dt)} \rangle^* \langle \phi_j^{(t+dt)} | \phi_k^{(t)} \rangle = \delta_{ik} \tag{38}$$

and

$$\boldsymbol{S}_E^{+}\boldsymbol{S}_E = \mathbf{1}. \tag{39}$$

Eq. (38) holds provided $\{\phi_j\}$ forms a complete set at time $t + dt$.

In practical calculations it is impossible in general to make the set $\{\phi_j\}$ complete. It is usually rather easy to select the important configurations, however. If an important configuration is omitted by mistake, this will show up in a decrease of the normalization integral, and the missing configuration then has to be found and added to the set. If the probability flows away through a large number of "uninteresting" configurations one may consider renormalization along the path Q.

5. Examples

For the sake of illustration of the theory we will apply it some examples with hydrogen atoms moving along given trajectories. The extended Hückel method [18] will be used with the overlap matrix equal to a unit matrix as is the custom in a number of semi-empirical methods. The dependence on Q of the basis functions has been ignored. In principle none of these approximations need to be introduced. Work is in progress to use *ab initio* methods. It is felt, however, that the level of accuracy chosen here is sufficient for a qualitatively correct result.

A typical nuclear velocity may be obtained from the $\mathrm{Fe(H_2O)_6^{3+}}$ complex of Ref. [8] with the vibrational frequency for the breathing mode $\nu_0 = 450\ \mathrm{cm}^{-1}$ 0.002 a.u. and reduced mass 18×1837 a.u. The maximum classical velocity in the lowest vibrational level may be obtained from:

$$\frac{Mv^2}{2} = \frac{\nu_0}{2} \tag{40}$$

and will give $v = 2.5 \times 10^{-4}$ as a bench mark.

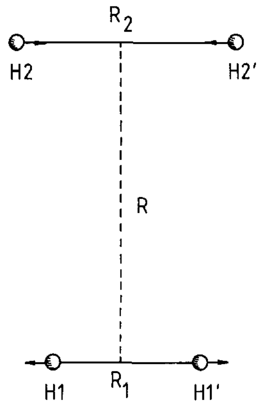

Fig. 3. Geometry and motion of the hydrogen nuclei

In the examples given below $H_2-H_2^+$ is arranged as in Fig. 3. The equilibrium distances are 1.4 a.u. for H_2 and 2.0 a.u. for H_2^+ [19]. The extended Hückel method, of course, cannot reproduce these values. We are primarily interested in what happens in the avoided crossing region and this region is qualitatively correctly reproduced for our purposes. The trajectory is defined by:

$$\begin{aligned} R_1 &= Q+1.2 \\ R_2 &= -Q+2.4. \end{aligned} \tag{41}$$

The avoided crossing occurs for $Q=0.6$ and $R_1=R_2=1.8$.

In the first example there is no medium between the two sub-systems. The system is prepared in the ground state at $R_1=1.20$ a.u. The electron probability density plots are given for a number of different values of v and R in Figs. [4, 5]. For $R=7$ a.u. the transfer is almost completely adiabatic for $v=1.0\times10^{-4}$. For $R=9$ the transfer probability is already very small for the same velocity. Since H_{12} decreases for increasing R roughly as given in Eq. (17), the probability for transfer also decreases rapidly. In the case of $v=10^{-5}$ the number of mesh points in the integration was ten times the number plotted in Fig. 5. Away from the crossing the wave length is smaller than the distance between the mesh points. This case is therefore an example of the problem discussed at the end of section 3.

The mechanism of electron transfer in the $H_2-H_2^+$ system is rather well simulating transfer in a redox system with metal ions. The nuclear motions in the two sub-systems are the cause of the transfer. It is of great importance to study how bridging atoms affect the transfer. In the next examples O^{2-} and S^{2-} ions are inserted between the H_2 systems (Figs. 6, 7). The transfer is now becoming almost adiabatic for $R=10$ a.u. and $v=2\times10^{-4}$ for O^{2-} and for $R=12$ and the same velocity for S^{2-}. The reason for the improved transfer is primarily the $2p$ and $3p$ orbitals of the bridge which decrease the energy of the antisymmetric combination. The energy gap thereby increases (see Fig. 8) leading to a larger transfer probability. This is the basis for a molecular orbital theory for electron

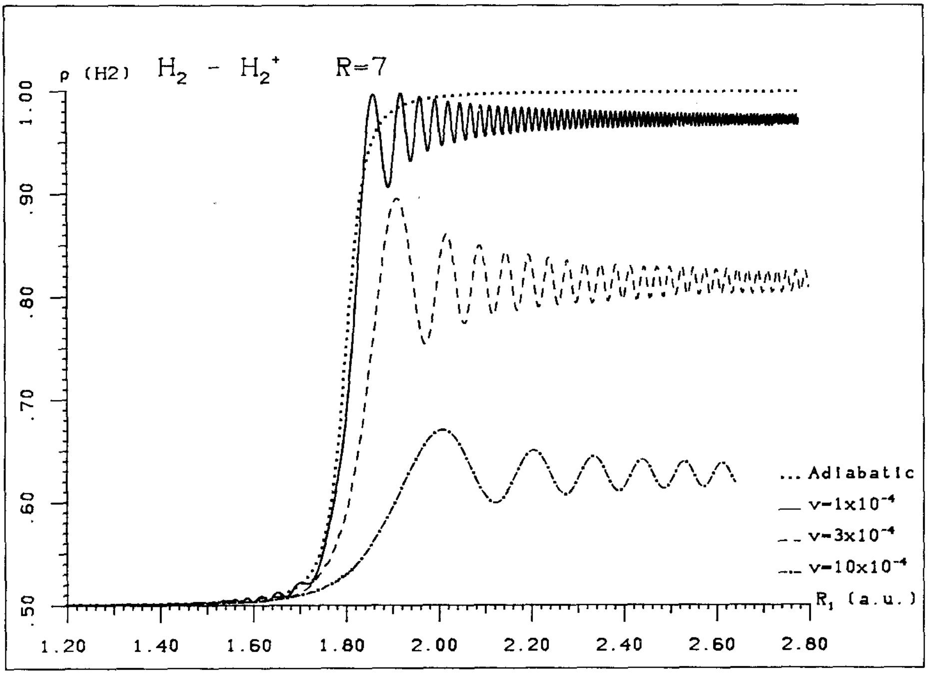

Fig. 4. Electron probability population at H2 (cf. Fig. 3) as a function of R_1 at different velocities for $R = 7$ a.u.

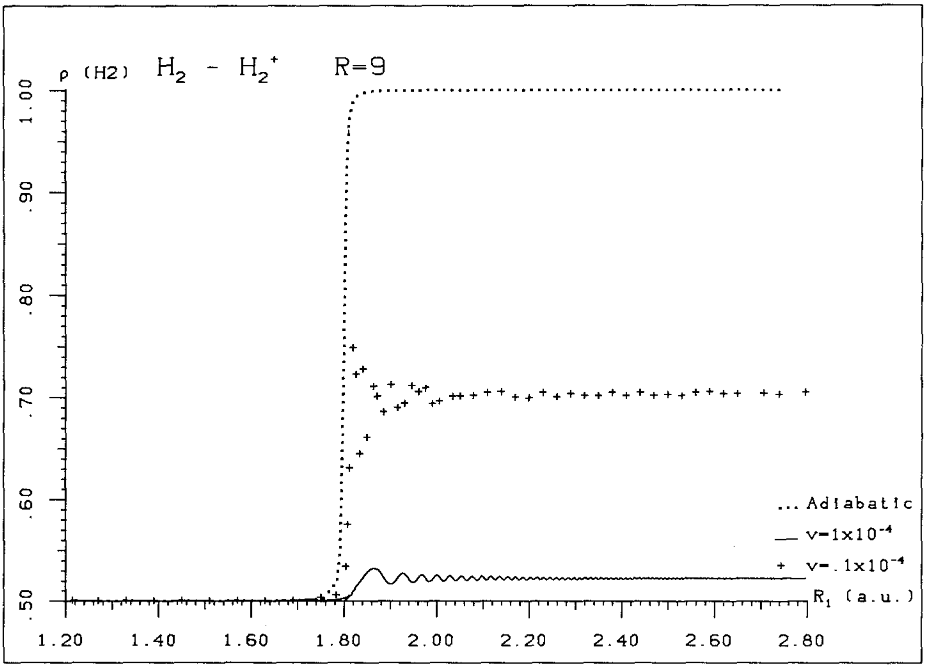

Fig. 5. Electron probability population at H2 (cf. Fig. 3) as a function of R_1 at different velocities for $R = 9$ a.u.

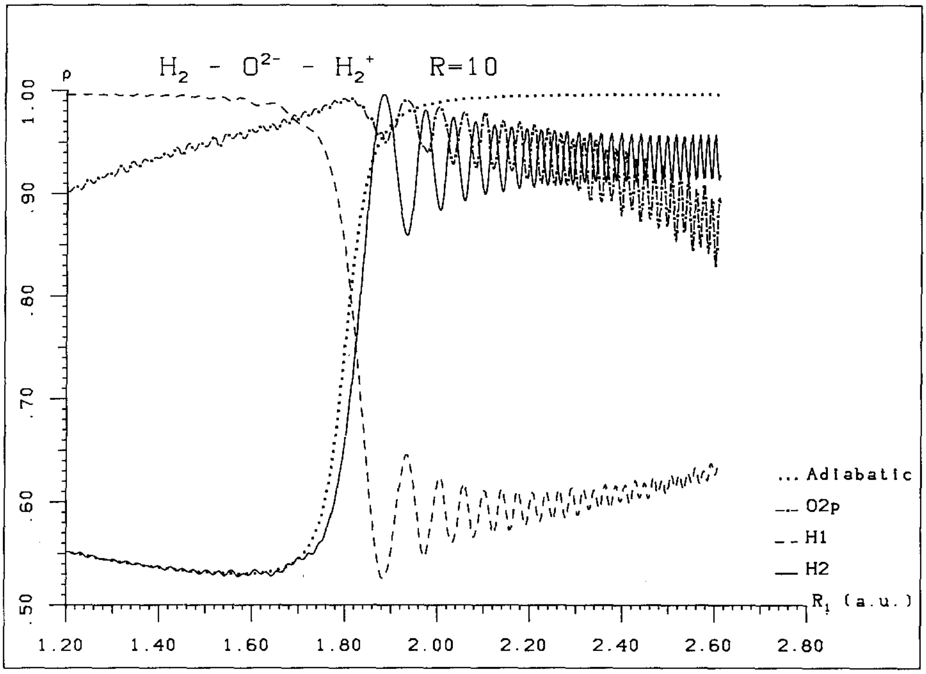

Fig. 6. Electron probability population at H2, the bridging O(2p) and H1 as a function of R_1; $v = 2\times10^{-4}$ a.u.; $R = 10$ a.u.

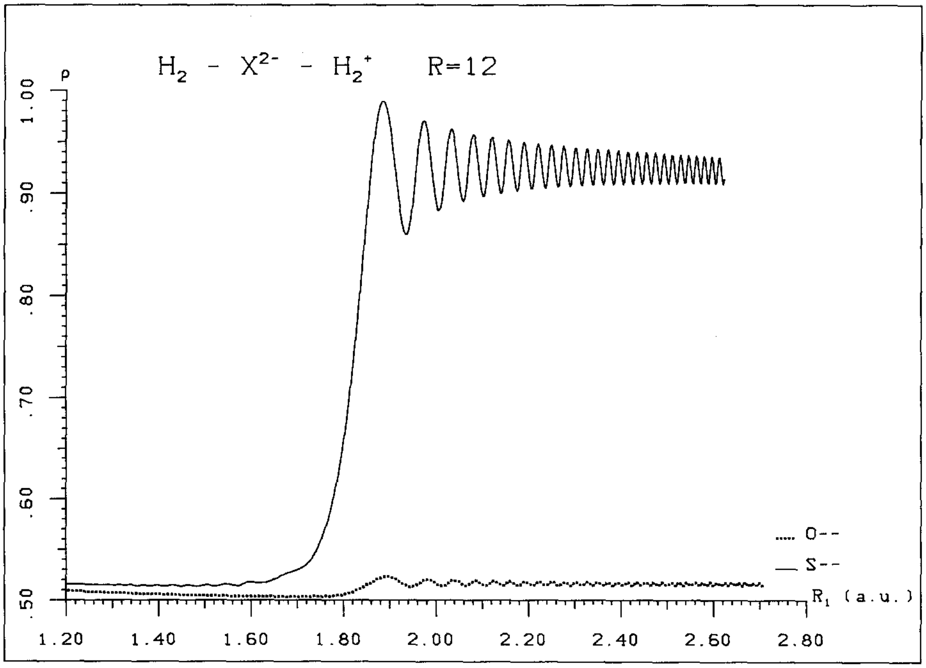

Fig. 7. Electron probability population at H2 for S^{2-} and O^{2-} as bridges at $R = 12$ a.u. and $v = 2\times10^{-4}$.

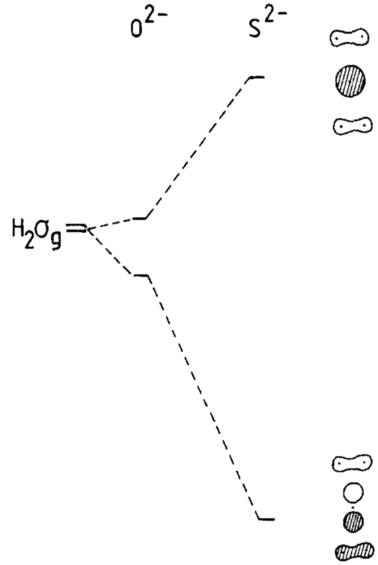

Fig. 8. Molecular orbital diagram for one intervening atom between the two H_2

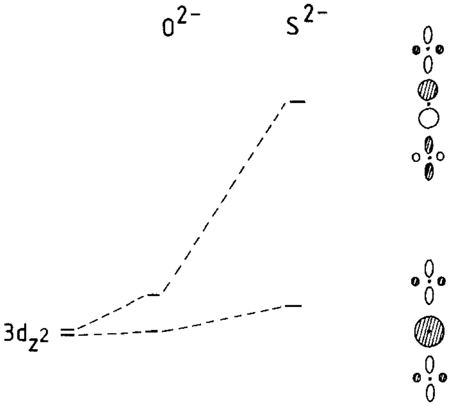

Fig. 9. Molecular orbital diagram for one intervening atom between two transition metal ion centers

transfer in the nonadiabatic limit [22]. The orbital energy diagram for the transferring orbitals in the case of transition metal ions is given in Fig. 9.

In the example given above O^{2-} and S^{2-} are only acting as mediators of electrons. It is of interest to study the case when the mediator has electrons at the same energy as the exchanging systems. One may therefore put another H_2 parallel to the other two and the distance R from each. Let us keep the interatomic distance of this H_2 equal to 1.8 (the value when $R_1 = R_2$). At a large velocity (5×10^{-4}) H_2^+ simply gets the electron from the bridging H_2 (Fig. 10), whereas for the smaller velocity the bridging H_2 manages to recover one electron from the end H_2 (Fig. 11). It may be noticed that the distance between the end H_2

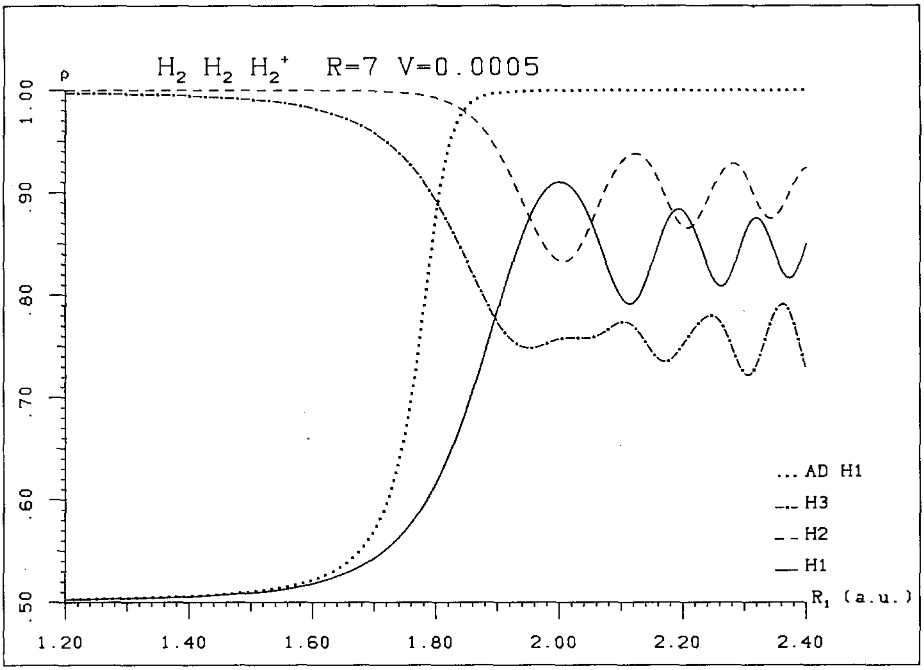

Fig. 10. Electron probability population at H1, H2 and H3 (of intervening H_2) as a function of R_1. $R = 7$ a.u. between each H_2; $v = 5 \times 10^{-4}$ a.u.

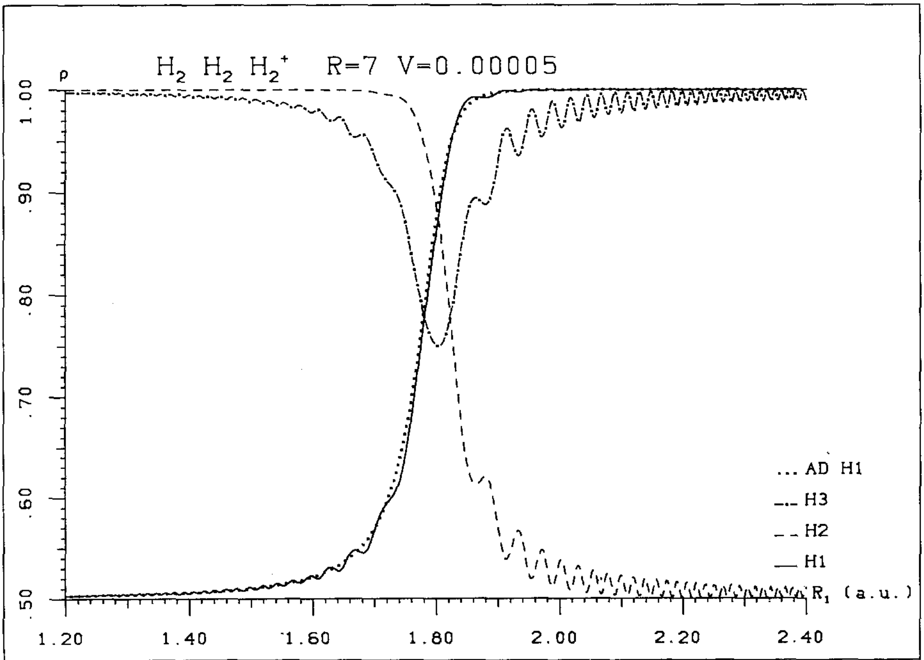

Fig. 11. Electron probability population at H1, H2 and H3 (of intervening H_2) as a function of R_1. $R = 7$ a.u. between each H_2; $v = 0.5 \times 10^{-4}$ a.u.

is now 14 a.u., i.e. twice as large as in the original example, but with only a small increase in non-adiabaticity. This is an example of "hole hopping" rather than "electron hopping". It is impossible for an electron to pass from the end H_2 to the end H_2^+ and "rest" on the intervening H_2. There is no molecular orbital available on the bridge H_2 for an additional electron. But an electron hole can be hosted for a finite time on the bridge. This type of electron transfer may be of importance in a number of systems, for instance organic semi-conductors.

6. Conclusion

By employing time dependent equations given by Nikitin [17] in quantum chemical calculations it is possible to gain some insight into electron transfer systems. The present work will be extended in two ways. One extension is to compare the extended Hückel method to more advanced methods on small systems, another to apply the extended Hückel method to larger systems of interest in chemical and biological systems.

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References

1. Chance, B., DeVault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. B., Sutin, N., eds.: "Tunneling in Biological Systems", Academic Press 1979
2. Marcus, R. A.: J. Chem. Phys. **24**, 966, 979 (1956); **43**, 679 (1965); Ann. Rev. Phys. Chem. **15**, 155 (1964)
3. Hush, N. S.: Trans. Farad. Soc. **57**, 557 (1961); Progr. Inorg. Chem. **8**, 391 (1967); Electrochem. Acta **13**, 1005 (1968)
4. Hopfield, J. J.: Proc. Natl. Acad. Sci. (USA) **71**, 3640 (1974); Biophys. **18**, 311 (1977)
5. Kestner, N. R., Logan, J., Jortner, J.: J. Phys. Chem. **78**, 2148 (1974)
6. Ulstrup, J., Jortner, J.: J. Chem. Phys. **63**, 4358 (1975)
7. Jortner, J.: J. Chem. Phys. **64**, 4860 (1976)
8. Brunschwig, B. S., Logan, J., Newton, M. D., Sutin, N.: J. Am. Chem. Soc. **102**, 5798 (1980)
9. Newton, M. D.: Int. J. Quant. Chem. **S14**, 363 (1980)
10. Orgel, L. E.: Report X Conseil Chim Solvay (Brussels 1956) p. 289
11. Halpern, J., Orgel, L. E.: Discuss Faraday Soc. **29**, 32 (1960)
12. Mayoh, B., Day, P.: J. Chem. Soc. (Dalton) **1973**, 846; Inorg. Chem. **13**, 2273 (1974)
13. Ratner, M. A., Ondrechen, M. J.: Mol. Phys. **32**, 1233 (1976)
14. Burdett, J. K.: Inorg. Chem. **17**, 2537 (1978)
15. Landau, L.: Z. Physik (USSR) **1**, 88 (1932); **2**, 46 (1932)
16. Zener, C.: Proc. Roy. Soc. (London) **A137**, 696 (1932); **A140**, 666 (1933)
17. Nikitin E. E.: in "Chemische Elementarprozesse". Ed. H. Hartmann (Springer Verlag 1968) p. 43; Adv. Quant. Chem. **5**, 135 (1970)
18. Hoffman, R.: J. Chem. Phys. **45**, 397 (1966)
19. Eyring, H., Walter, J., Kimball, G. E.: "Quantum Chemistry" (John Wiley, 1965), p. 198
20. Hirsch, G., Bruna, P. J., Buenker, R. J., Peyrimhoff, S. D.: Chem. Phys. **45**, 335 (1980)
21. Löwdin, P.-O.: Adv. Quant. Chem. **3**, 323 (1967)
22. Larsson, S.: J. Am. Chem. Soc. **104**, 000 (1981)

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