Comparison between Intervalance Charge Transfer and Molecular Tautomerism

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Abstract

The charge exchange process in the intervalence (mixed-valence) system is interpreted in terms of the nonstationary state mechanism which is a well-known approach for rationalizing the molecular tautomerism process. The two kinds of processes are viewed in a close analogy in the sense that both involve a pair of near-degenerate levels in a double-well potential. However, a comparison is made between the two cases to demonstrate that an electron moves not only faster but also farther in distance than a nucleus does.

1. Introduction

Various intervalence (mixed-valence) molecular species have been synthesized for the interest of their unique electronic properties [1–3]. The main structural feature of such molecular species is two identical metal–ion complexes of different oxidation states connected by a bridging ligand. Typical example is μ-pyrazine–decammine diruthenium (5+) ion

\[
\begin{align*}
\text{Ru}^{II} & \quad \text{N} \quad \text{N} \quad \text{Ru}^{III} \\
\end{align*}
\]

Of particular interest for these systems was the phenomenon of electron exchange process described by electronic alternating jump between the two metal sites

\[ [\text{Ru}(II), \text{Ru}(III)] \leftrightarrow [\text{Ru}(III), \text{Ru}(II)]. \]

As suggested by some recent experiments, the time scale of such process is shorter than the IR time scale \(10^{-13} \text{ sec}\), but longer than the ESCA time scale \(10^{-15} \text{ sec}\) [1].

In this paper, to account for the exchange process, a simple model is presented in which an electron is moving in a double-well potential located at the metal sites. This model is analogous to the one describing the other type of double-well problem like molecular tautomerism, one familiar example being ammonia inversion process. Certainly, the moving electron in the present system is a much lighter particle than a nucleus in the molecular tautomerism case. It is of great interest for us to seek the similarities and differences between the two cases.

The vibrational or vibronic effect is ignored in this model, in view that the time scale of the charge exchange process is shorter than that of molecular vibration.
Therefore, in the time scale of the electronic motion, the nuclei are nearly stationary. Thus the nuclear motion is not expected to play an important role in the charge exchange process and only the electronic effect is considered. The approximation is in a similar sense as the Franck–Condon principle.

2. Nonstationary State Mechanism

A pair of near-degenerate electronic states \( \phi_{\pm} = \phi_a \pm \phi_b \) (defined at a fixed nuclear configuration \( Q^0 \)) appears to be crucial for the charge transfer process. Here \( \phi_a \) and \( \phi_b \) are the two valence atomic orbitals at the metals and the contribution to \( \phi_{\pm} \) from the ligands is ignored in the first approximation. The energy splitting between the pair of states can be expressed by the matrix element between the two localized functions, \( \phi_a \) and \( \phi_b \), i.e.,

\[
(E_- - E_+) = 2 \langle \phi_a | H | \phi_b \rangle.
\]

The small energy splitting is due to a large separation and hence a small overlap between the two valence orbitals at the metals.

To account for the charge exchange process, we consider the possibility that the electronic wave function being prepared in a nonstationary state under a photoexcitation condition

\[
\psi_{\text{el}}(q,t) = \phi_+ e^{-iE_+t/\hbar} + \phi_- e^{-iE_-t/\hbar}.
\]  

(1)

In the time development of such a nonstationary state, the probability that the system will shuttle back and forth between the states described by the localized functions \( \phi_a \) or \( \phi_b \), with the frequency \( (E_- - E_+)/\hbar = 2 \langle \phi_a | H | \phi_b \rangle/\hbar \). The time scale of the charge exchange process of the mixed-valence system is in the range of \( 10^{-14} \) sec which corresponds to a \( \Delta E \) value about 1–10 kcal/mol. It is noted that only when the charge transfer frequency \( (\Delta E/\hbar) \) is much larger than the vibrational frequency (one order of magnitude larger in the present case), it is justified to consider the electronic part of wave function only as given by Eq. (1) with some fixed nuclear configuration \( Q^0 \).

One may wonder why the possibility of a stationary state mechanism is not considered where the electronic wave function is given as

\[
\phi_{\text{el}}(q,Q) = C_+(Q) \phi_+(q,Q^0) + C_-(Q) \phi_-(q,Q^0).
\]  

(2)

The basis functions \( \phi_{\pm}(q,Q^0) \) are referred to those at the fixed nuclear position (crude BO basis) with a symmetrical nuclear configuration. This mechanism describes a vibrationally induced configuration mixing and hence the charge transfer process, analogous to the Herzberg–Teller effect for intensity borrowing mechanism. The difficulty with this mechanism is its prediction on the charge exchange rate being equal to or less than the vibrational frequency \( (10^{13} \text{ sec}^{-1}) \). This contradicts the fact that the charge exchange rate is known to be faster than the vibrational frequency.

Since the nonstationary state mechanism is a well-known approach for describing the molecular tautomerism process, therefore, a close analogy to Eq.
can be given by the vibrational wave function, for example, describing the ammonia inversion process [4]

\[ \psi_{\text{vib}}(Q,t) = \chi_+ e^{-iE_+t/\hbar} + \chi_- e^{-iE_-t/\hbar}. \]  

(3)

Analogous to our previous electronic problem, a pair of near-degenerate vibrational levels \( \chi_\pm \) in the double-well potential can be described approximately as symmetrical and antisymmetrical combinations of the two local Gaussians, i.e., \( \chi_\pm \approx \chi_a \pm \chi_b \) [5]. Certainly, one obvious difference is that Eq. (3) describes the nuclear alternating jump between the two sites, while Eq. (1) describes the electronic one.

3. Comparison between Electronic Motion and Nuclear Motion

Here we would like to demonstrate some different behavior between an electron and a nucleus, each moving in a double-well potential. First, one assumes that the functions of a near-degenerate pair \( \phi_\pm = a \pm b \) are applicable to both the electronic and vibrational cases. Here \( a \) and \( b \) are referred to the atomic orbitals at metals in the former, and local Gaussian functions in the latter. The energy splitting between the two levels is proportional to \( H_{ab} = \langle a | H | b \rangle \) which can be estimated by way of the Mulliken approximation for both cases. The approximation is adequate for our order-of-magnitude estimation. One then obtains the rate expression in a simple form

\[ K = \frac{\Delta E}{\hbar} \approx \frac{(H_{aa}/\hbar)S_{ab}}{S_{ab}}, \] 

(4)

where \( S_{ab} \) can be approximated by an exponential factor as shown in the latter and \( H_{aa}/\hbar \) corresponds to a frequency factor similar to that in the usual kinetic rate expression. The ratio between the two frequency factors of the electronic case and of the vibrational case can be shown approximately equal to the square root of the mass ratio between nucleus and electron \( (m_n/m_e)^{1/2} \) [6]. Then one concludes that a charge exchange process is generally one to two orders of magnitude faster than a molecular tautomerism process, if the values of the exponential factor \( S_{ab} \) are assumed equal in the two cases. We will show next that the same value of \( S_{ab} \) will allow larger separations between \( a \) and \( b \) in the electronic system. Let us demonstrate it by considering a double-well potential [4] in the simple form \( V(Q) = \frac{1}{2}K(|Q| - R/2)^2 \) for the vibrational system such as ammonia inversion process (see Fig. 1). For the two Gaussian functions \( a \) and \( b \) separated by a distance \( R \), the overlap \( S_{ab} \) has the explicit form exp\((-KR^2/\hbar^2)\).
Here $\hbar \omega$ is the vibrational quanta for the single minimum potential $KQ^2/2$. The factor $\frac{1}{2}KR^2/\hbar \omega$ can be interpreted as the ratio of the energy barrier [barrier = $V(0) = \frac{1}{2}K(R/2)^2 = \frac{1}{2}KR^2$] to the zero-point vibrational energy $\hbar \omega/2$. One can easily see that the exponential factor $S_{ab}$ in the vibrational case falls off rather fast as $R$ increases. For the mixed-valence system with two charge trapping centers at the metals, the electronic Hamiltonian with a double-well potential, can be given as $T_q + \xi/|q - R_a| + \xi/|q - R_b|$, similar to that for the $\text{H}_2^+$ system. The overlap $S_{ab}$ between the two atomic orbitals has the general form $[\Sigma_{k=1}^N C_k (\zeta R)^k e^{-\xi R}]$ [7], with $\zeta$ and $R$ denoting the effective nuclear charge and the distance between the metals, respectively. The dominating factor in the overlap expression $\exp(-\zeta R)$ falls off relatively slow as $R$ increases. The factor $\xi R$ can be interpreted as the ratio of the distance between the two sites ($R$) to the “size” of the atomic orbital (1/\zeta). The different behavior between the overlaps simply reflects the fact that the Coulomb potential in the electronic case increases less steeply than the harmonic oscillator potential does in the nuclear case in the long range region. In addition, in the Coulomb potential case, the steepness of the short range behavior near the nuclei is unimportant, in view of the fact that the atomic orbitals of high $l$ such as $d$ and $f$ orbitals have a low amplitude there. One physical consequence of this is the short range for molecular tautomerism process, usually in the order of only one bond distance. On the other hand, for the charge transfer process in the mixed-valence system, electron can often move over a distance several bond lengths apart. It appears that the ligands also take part in extending the moving distance of the charge transfer process in this system.

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Bibliography


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