QUANTUM THEORY OF CHEMICAL REACTIONS
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OF
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I. Collision Theory, Reaction Path, Static Indices

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This treatise is devoted to an analysis of the present state of the quantum theory of chemical reactions.

It will be divided into three volumes and will contain the contributions to an international seminar organized by the editors.

The first one, is concerned with the fundamental problems which occur when studying a gas phase reaction or a reaction for which the solvent effect is not taken into account.

The two first papers show how the collision theory can be used to predict the behaviour of interacting small molecules.

For large molecules the complete calculations are not possible. We can only estimate the reaction path by calculating important areas of the potential surfaces. Four papers are concerned with this important process. Furthermore, in one of these, the electronic reorganization which occurs along the reaction path is carefully analyzed.

Two papers are devoted to the discussion of general rules as aromaticity rules, symmetry rules.

The last two papers are concerned with the electrostatic molecular potential method which is the modern way of using static indices to establish relations between structure and chemical reactivity.

Volume II will be devoted to a detailed analysis of the role of the solvent and volume III will present important applications as reaction mechanisms, photochemistry, catalysis, biochemical reactions and drug design.
SOME RECENT DEVELOPMENTS IN THE MOLECULAR TREATMENT OF ATOM-ATOM COLLISIONS.

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INTRODUCTION

Since a few years, we have been applying (at the C.M.O.A. 1 in Paris and at the L.C.A.O. 2 in Orsay) Molecular Physics Methods to the study of atom-atom or ion-atom collisions at low and moderate energies (from few eV to few keV). The procedure is somewhat similar to that used in the study of Electronic Spectra of Diatomic Molecules. Indeed, in the velocity range under consideration, electrons move generally much faster than the nuclei which suggests to find approximate electronic wavefunctions for the clamped nuclei problem. These functions, in turn, serve as an expansion basis for expressing the total wavefunction that describes both the electrons and the nuclei of the system. The study of an atom-atom collision problem then requires the resolution of a more or less large set of coupled equations. These equations determine the nuclear wavefunctions whose asymptotic behavior yield the scattering amplitudes and consequently the cross sections.

Actually, since a collision problem differs from a bound diatomic molecule in the spatial extension of the nuclear motion and in the velocity of the nuclei, the standard procedure of finding adiabatic Born-Oppenheimer (BO) wavefunctions is not necessarily the most appropriate starting point. Indeed, viewed in this framework, electronic transitions (which can occur in various ranges of internuclear distances R) are induced by non adiabatic dynamical terms involving the radial and rotational nuclear velocities (-\(\nabla_R\)). These terms might be so large that the original assumptions of the BO approximation breakdown. In fact, since the problem generally amounts to solve a set of coupled equations in a given subspace, any expansion basis in this subspace could equally well be used. The problem then turns out to be that of defining a meaningful reduced set of states accounting for the largest part of the interactions and amenable to practical calculations. The problem of defining diabatic states is to be placed in this context. In practice, when choosing the basis of electronic wavefunctions one should particularly consider:

a) the range of internuclear distance where the transitions are

susceptible to occur,
b) the relative importance of the different interactions in this range (e.g. the various Hund's cases),
c) the radial velocity of nuclei in the transition region.

The following examples will provide some illustrations of these ideas and are intended to sample the general lines along which we are developing the research in this field.

DIABATIC STATES AND INELASTIC PROCESSES IN HE$^+$ + HE COLLISIONS

The He$^+$ + He collision offers a large variety of excitation mechanisms and the methods developed to handle these processes are illustrative of some aspects of the molecular treatment of atomic collision.

It was first pointed out by Lichten$^3$ that the two lowest $^2\Sigma^+$ and $^2\Sigma^+$ BO adiabatic states of the He$_2^+$ molecule ion could not account for the large resonant charge transfer process of the He$^+$ + He collision at moderate energies. The area between the corresponding potential energy curves, entering the charge transfer probability as

$$P_{CT} = \frac{1}{2} \sin^2 \left( \frac{1}{\nu} \int (E_{\Sigma g} - E_{\Sigma u}) \, dR \right)$$

was indeed found to be too small. This situation led Lichten$^3$ to suggest another approach based on single configuration states built from molecular orbitals (MO). These states were termed diabatic states. In that picture (Fig. 1), the $^2\Sigma^+_g$ and the $^2\Sigma^+_u$ states issuing from He$^+$ (ls) + He(ls$^2$) have respectively the (ls$^2$ g$p_0^2$) and the (ls$^2$ g$2p_0^2$) configurations.

![Fig. 1](image.png)

Fig. 1 Scheme of the correlation diagrams for the MO and the states of the He$^+$+He system. The MO diagram also illustrates the general correlations of the low-lying orbitals in a symmetric system.
As \( R \) decreases and tends to zero, the \((1s\sigma, 2p\sigma^2)^2\Sigma^+\) core excited state correlates with the \(1s2p^2\) auto-ionizing configuration of the \(Be^+\) ion. On its way in, the corresponding energy curve crosses the infinite \((1s\sigma^2 n\Sigma^0) \Sigma^+\) Rydberg series as well as the associated continuum \((1s\sigma^2 \phi_{n\Sigma^0} g_{\Sigma^+}) \Sigma^+\). These crossings (later called diabatic II crossings) occur around the distance where the MO energy differences (\(\epsilon_1\)) are such that (Fig. 2)

\[
\epsilon_{2p\sigma^u} - \epsilon_{1s\sigma^g} = \epsilon_{n\Sigma^0} - \epsilon_{2p\sigma^u}
\]

Fig. 2. General scheme for diabatic II crossings. A vacancy is present in the inner MO (A) and gives rise to the core excited configuration state (AB\(^2\)). This state crosses the Rydberg series (A\(^2\)C) when:

\[2\epsilon_\text{B} = \epsilon_\text{A} + \epsilon_\text{C}\]

This situation always occurs in rare gas\(^+\) + rare gas collisions.

According to the Wigner-Von Neumann theorem these crossings will appear as avoided crossings in the adiabatic BO representation. Consequently, the area between the \(2\Sigma^+\) and the \(2\Sigma^+\) energy curves, correlated with the \(\text{He}(1s) + \text{He}(1s^2)\) level, is smaller when calculated with the adiabatic curves than with the diabatic curves. The failure of the adia-
adiabatic approach to account for the simple resonant charge transfer process is due to the neglect of higher lying adiabatic states. Indeed, at each avoided crossing (Fig. 3),

\[ \begin{align*}
\{I, \Delta\} & \quad \text{diabatic} \\
R & \\
\text{diabatic} & \quad \text{adiabatic}
\end{align*} \]

\[ H_{ij} \]

\[ d/dR \]

Fig. 3. At each crossing between the diabatic curves (a) the states are weakly coupled by the electronic hamiltonian. At each avoided crossing between the adiabatic curves (b) the states are strongly coupled by \( d/dR \) matrix elements. In (a) \( \Gamma \) and \( \Delta \) are the width and the shift of a level imbedded in a continuum.

the adiabatic wave function displays rapid variations with \( R \), as the configuration changes from e.g. \((1s_\sigma, 2p_\sigma^2)\) to \((1s_\sigma^2 n\ell_\sigma)\). Huge non adiabatic couplings \((\langle i | d/dR | j \rangle = 15 \text{a}^{-1}\)) between the \( 2p_\sigma^+ \) states then require inclusion of all higher Rydberg states as well as the associated continuum! (Fig. 3). The treatment of elastic and resonant charge transfer scattering would be completely intractable in such a representation. On the other hand, the single configuration diabatic states \((1s_\sigma, 2p_\sigma^2)\) \( 2p_\sigma^+ \) and \((1s_\sigma^2 n\ell_\sigma^2)\) \( 2p_\sigma^+ \) cancel all of the \( d/dR, d^2/dR^2, L^+L^- \), matrix elements as shown in ref. 6. The only remaining interaction is due to inter-electronic repulsions (electronic correlation):

\[ \langle 1s_\sigma^2 2p_\sigma^2 | \sum_{i<j} 1/r_{ij} | 1s_\sigma^2 n\ell_\sigma \rangle \approx 3 \times 10^{-2} \text{ Hartree} \]

Comparison of the couplings, in the adiabatic \((v_R \langle i | d/dR | j \rangle)\) and diabatic \((\langle i | H_{ij} | j \rangle)\) representations, shows that for all nuclear radial velocities larger than \( v_R = 2 \times 10^{-3} \text{ a.u.} \) the diabatic single configuration description has to be preferred. This representation actually enables the description of the system as undergoing essentially elastic scattering slightly perturbed by inelastic transitions at curve crossings. This, in turn, allows the use of two state approximations (as e.g. the simple Landau-Zener-Stueckelberg approximation\(^7\), the distorted wave approximation\(^6\) and two-
state quantal close coupling treatments\textsuperscript{8} for treating excitation, charge transfer and ionization processes of the type:

\[
\text{He}^+(1s) + \text{He}(1s^2) \rightarrow \text{He}^+(1s) + \text{He}(l_{\text{snf}}) \rightarrow 2\text{He}^+(1s) + e^-
\]

at a few hundred eV collision energies. Such electronic transitions at curve crossings are known to yield oscillations in the differential cross sections arising from the interference between the waves scattered by the two accessible potentials inside the curve crossing (Fig. 3).

As the collision energy reaches the keV energy range, experiments\textsuperscript{9, 10} show the selective single and double excitation of the n=2 levels of He.

![Diagram](image.png)

**Fig. 4.** Schematic view showing that after the sudden rotation of the internuclear axis (0 $\rightarrow$ 0) the $\sigma$ MO becomes a mixture of $\sigma$ and $\pi$ MO's.

Following an idea of Bates and Williams\textsuperscript{11}, McCarrol and Piacentini\textsuperscript{12}, invoked a rotational coupling at small R between states involving the closely lying $2p\sigma_u$ and $2p\pi_u$ MO's (Fig. 1) namely:

\[
(1\sigma_g 2p\sigma_u^2)_{\sigma}^{2}\Delta_g - (1\sigma_g 2p\sigma_u 2p\pi_u^\Pi)_{\sigma}^{2}\Delta_g - (1\sigma_g 2p\pi_u^\Pi)_{\sigma}^{2}\Delta_g
\]

\[
(1\sigma_g 2p\sigma_u^2)_{\pi}^{2}\Pi_u - (1\sigma_g 2p\pi_u^\Pi)_{\pi}^{2}\Pi_u
\]

Rotational coupling is known to occur at small impact parameters (b) and small R, where the rapid rotation of the internuclear axis lets no time for the electrons to readjust adiabatically. A $\sigma$ MO, before the rotation of the internuclear axis, then becomes a mixture of $\sigma$ and $\pi$ MO's, after the axis flipping (Fig. 4). This situation yields a $\sigma \leftrightarrow \pi$ transition which is induced by the component of the electronic angular
momentum perpendicular to the collision plane \((L_y)\). Semi-classically this coupling writes:

\[ v_o b <\sigma |L_y|\pi>/R^2, \]

\(v_o\) being the relative nuclear collision velocity.

The \(2p\pi\) MO which correlates with \(\pi\) \(2p\) atomic orbitals (AO), Fig. 1, thus provides a selective route for populating the \(n=2\) levels of He.

Only recently have the potential energy curves of the \(He^+\) molecule been calculated\(^1\), for small \(R\), to handle this problem. In order to avoid the linear dependances appearing at small \(R\) among LCAO-MO wavefunctions, a one-center expansion\(^5,\,14,\,15\) was used and joined to the two-center results at larger \(R\) (\(\geq 0.5\ \text{a}\)). Actually, such a procedure, which might introduce discontinuities, can be avoided as recently discussed by Gauyacq\(^6\). It suffices to add united atom AO's to the two-center expansion basis. When, for example, the \(1s\) and \(1s\) orbitals become almost linearly dependent the ungerade combination can be deleted provided the proper 2p AO's for the united atom have been included in the expansion basis on both the two centers.

To treat the excitation process via rotational coupling at small \(R\) it might seem, at first sight, that a set made of 2-\(u\) states and a set of 4-\(g\) states would suffice. Furthermore, since the two \((1s\sigma\ 2p\sigma\ 2p\pi\ 2\Pi)\) states can be built in such away that only one of them, \(\text{namely} (1s\sigma\ (2p\sigma\ 2p\pi\ u\ 1\Pi) \ 2\Pi\ g\ u)\), couples rotationally with the incident \((1s\sigma\ 2p\sigma\ 2\Pi)\) state only three states in the gerade set would suffice. Actually this view is too naïve since it does not take into consideration an important drawback of the single configuration description based on the LCAO-MO approach in symmetric systems. Since a \(g\) or \(u\) orbital dissociates on both of the two He centers, one gets in the dissociation of e.g. the considered \((1s\sigma\ (2p\sigma\ 2p\pi\ u\ 1\Pi) \ 2\Pi\ g\ u)\) state a mixture of the following separated-atom states:

\[
\begin{align*}
\text{He}_A^+ + \text{He}_B^\times (1s\ 2p\ 3\Pi) \\
\text{He}_A^+ + \text{He}_B^\times (1s\ 2p\ 1\Pi) \\
\text{He}_A^\times + \text{He}_B^- (1s^2\ 2p\ 2\Pi) \\
\text{He}_A^\times (n=2) + \text{He}(1s^2\ 1S)
\end{align*}
\]

and the same with interchange of \(A\) and \(B\) (see similar examples in ref.\(^4,\,6,\,15,\,16\)). This means that there exist three other configuration state functions:

\[
\begin{align*}
(1s\sigma\ (2p\sigma\ 2p\pi\ \ 3\Pi\ g\ u\ u\ 2\Pi\ g) \\
(1s\sigma^2\ 3d\pi\ \ 2\Pi\ g\ g) \\
(2p\sigma\ 3d\pi\ \ 2\Pi\ u\ g)
\end{align*}
\]
which interact at large $R$ with the considered $^2\Pi_g$ state (Fig. 5).

Fig. 5. Schematic dissociation and couplings of some $^2\Pi$ states involved in the rotational coupling mechanism of the He$^+$ + He system. (CSF stand for configuration state functions).

The same difficulty occurs with the $^2\Pi$ and the $^2\Delta$ states. This situation prevents from extracting the scattering $S$ matrix once the primary rotational excitation of the $^2\Pi_g$, $^2\Delta_g$ and $^2\Pi_u$ states has been solved. It might thus seem that either of a $g$-fold configuration interaction
(CI) in each of the considered symmetries, or a valence bond (VB) description would be more appropriate at large separations. Unfortunately, the VB approach suffers from similar defects to those discussed above, but at small R. Furthermore, if CI wavefunctions are used, non adiabatic d/dR couplings appear in each of the above 4-fold subspaces reflecting the change of the wavefunctions from a molecular (LCAO) description to an atomic (VB) description (Fig. 5). Consequently, there exists a range of R values where none of single configuration or CI wavefunctions can reduce the problem to less than $4-2\Sigma^+$, $4-2\Delta$, $4-2\Pi$ states. In practice, however, at relatively low velocities, non adiabatic coupling might become negligible and the major part of the excitation will go adiabatically into one of the states in each symmetry. In contrast, at very high velocities the populated states will suddenly project on to all of their atomic components. In the intermediate regime under consideration, the initial population will be more or less shared between the various atomic components of the type discussed above. Therefore, all of the state involved in the dissociation region have to be considered.

In order to avoid the sharply peaking d/dR matrix elements arising in the adiabatic CI approach, it suffices to integrate the scattering-closed-coupled equations in the single configuration LCAO-MO representation up to a sufficiently large value of R. In this representation, the states have no d/dR coupling matrix elements since they differ by at least two spin orbitals. Although, at large R, such states give rise to large off diagonal Hel matrix elements, these couplings tend to constant values in the asymptotic region. Consequently, in this region, constant linear combinations of the diabatic states yield the proper non interacting atomic states without introducing any cumbersome d/dR contribution. In practice, this transformation is carried out during the integration of the scattering equations, just before extracting the S matrix. The Gordon integration method actually enables this procedure, to be easily achieved. Indeed, since in this method the equations are locally transformed, at each integration step, from the diabatic to the (local) adiabatic representation and then back to the diabatic one, it suffices to stay in the adiabatic basis once R gets large enough.

Fig. 6 shows the results of the above procedure in the treatment of the He(1s 2p $^3,^1p$) excitation via rotational coupling in He$^+ +$ He.
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Fig. 6. Reduced differential cross section \( \rho = \theta \sin \theta \sigma(\theta) \) as functions of the reduced angle \( \tau = E\theta \), for the \( 2^1P(-) \) and \( 2^3P(-) \) direct excitations of He in He\(^+\) + He collisions at \( E_{\text{Lab}} = 2 \) keV. The sum of these theoretical cross sections \( \rho_{\text{TH}}(-) \) is to be compared with experiment \( \rho_{\text{EXP}} \).

This procedure has also been applied by Gauyacq\(^{21}\) to the study of the single and double excitations of levels involving the 2s and 2p orbitals of He in He + He collisions at keV energies. In addition, the dissociations into unstable negative ions of the type He\(^-\)(1s\(^2\) 2p) and into doubly excited states were considered\(^{21}\) in some detail in order to assess the contribution of such species to the ionization processes of this system.

CHARGE TRANSFER PROCESSES IN H\(^+\) + RARE GAS COLLISIONS\(^ {22,23}\): H\(^+\) + KR.

The experimental work on H\(^+\) + Kr collisions demonstrated that total charge transfer cross sections amounting to several A\(^2\) could be obtained at collision energies as low as a few hundred eV. Among the various charge transfer processes the near resonant one:
\[ H^+ + Kr(4p^6 1S_o) \rightarrow H(2S_{1/2}) + Kr^+(4p^5 2P_{3/2}); \quad \Delta E = 0.4 \text{ eV} \]

\[ \rightarrow H(2S_{1/2}) + Kr^+(4p^5 2P_{1/2}); \quad \Delta E = 1.06 \text{ eV} \]

is the most privileged an was recently submitted to detailed experimental differential studies\textsuperscript{23}.

In order to provide the basis for a molecular study of this process, we have performed a set of calculations on some states of the \((H-Kr)^+\) molecule ion\textsuperscript{24}. Since single configuration wavefunctions usually provide a good starting point, SCF calculations were first carried out on the ground state \(\ldots 8\sigma^2)X^1\Sigma^+\) configuration and some singly as well as doubly excited states were determined in the virtual orbital approximation. CI calculations limited to \(28\ldots 1\Sigma^+\) states were also performed in order to obtain a more reliable ground state potential curve. This potential was subsequently used in low energy \((E < 20 \text{ eV})\) elastic cross section calculations and quite satisfactory agreement with experiment was achieved\textsuperscript{23}.

As to inelastic processes, investigation of the coupling term between the \(\ldots 8\sigma^2) X^1\Sigma^+\) ground state (correlated with \(H^+ + Kr(4p^6)\)) and the lowest \(\ldots 4\pi^3 8\sigma^2 9\sigma) I^1\Pi\) configuration state (issuing from \(H(1s) + Kr^+(4p^5)\)) showed that rotational coupling should be inefficient in inducing the charge transfer process. Although spin-orbit interactions should be considered to investigate the population of the \(2^p_{1/2}\) and the \(2^p_{3/2}\) sublevels of \(Kr^+\), their effect is found to be much too small to have a significant influence on the primary excitation mechanism from the \(X^1\Sigma^+\) state. Next, as the \(X^1\Sigma^+\) state and the first excited \(\ldots 8\sigma 9\sigma) I^1\Pi\) state differ from each other by one MO, a \(d/dR\) coupling does exist between the two states:

\[ <X^1\Sigma^+|d/dR|I^1\Pi> = \sqrt{2} <8\sigma|d/dR|9\sigma> \]

(the \(8\sigma\) and \(9\sigma\) MO's being respectively correlated with \(\sigma 4p^5_{Kr}\) and \(\sigma 1s_H\)). Unfortunately the related dynamical coupling \((v_R|d/dR|I^+\) amounts at most to 15% of the \(X-I\) energy difference at \(E = 100 \text{ eV}\). This is insufficient to fully account for the observed large total charge transfer cross sections at this energy. In addition, since the SCF calculation was performed on the ground state closed-shell configuration, the Brillouin theorem states that no direct coupling is induced by the electronic hamiltonian between the considered \(X\) and \(I\) states. However, as the \(X\) and \(I\) states lie very close to each other, at large \(R\), second order interactions should also be considered. Particularly it is found\textsuperscript{24} that both the \(X\) and the \(I\) states predominantly interact with the doubly excited \(\ldots 9\sigma^2) D^1\Sigma^+\) state which dissociates into \(H^-(1s^2) + Kr^{2+}(4p^4)\) \((\sqrt{2} 1D + 1S)/\sqrt{3}\) (Fig. 7). From perturbation theory, it it estimated that the interaction between the \(X\) and \(I\) states, via the doubly excited \(D^1\Sigma^+\) relay state, may become of the same order of magnitude as the \(X-I\) energy difference around \(R = 6a_0\). Such an interaction at large \(R\) can indeed yield an important total cross section and should induce the
major part of the charge transfer transitions.

Considering this effect together with the spin-orbit interaction (see further discussions below) in a four-state quantal close coupling treatment, we obtained qualitative agreement with the measured differential cross sections\textsuperscript{23} and only about 60% of the total experimental charge transfer cross section\textsuperscript{25}. Hence, our neglect of the radial dynamical coupling was not completely justified since it resulted in significant discrepancies in the comparison with experiment.

However, the calculation of the d/dR matrix element as a function of R is an expensive task requiring twice as much effort as that necessary to determine the energy curves. In addition, there exist, to our knowledge, no efficient programs to handle such a coupling (involving first derivative terms) in quantal close coupling calculations. Furthermore, the introduction, in our approach, of the D\textsubscript{1}Σ\textsuperscript{+} relay state, which is negligibly populated, means that we have failed in adequately describing the process. Intuitively, a more appropriate description would confine the interactions to the lowest Σ\textsuperscript{+} states without calling for any extra (virtual contribution).

As the charge transfer transitions occur at large R (6-7\textalpha\textsubscript{0}), it seems that a description in terms of atomic orbitals in a valence bond (VB) approach could provide a better starting point\textsuperscript{26}. Considering the VB states issuing from H\textsuperscript{+} + Kr and H + Kr\textsuperscript{+}, one has respectively the following configuration state functions:

\[
|\ldots\ldots σ^4p_{Kr} \bar{σ}^4p_{Kr}| /\sqrt{2} \{ |\ldots\ldots σ^4p_{Kr} \bar{σ}1s_{H}| - |\ldots\bar{σ}^4p_{Kr} σ1s_{H}| \}
\]

In this two-fold subspace one may choose two arbitrary orthonormal states. Using Schmidt orthogonalization we can build the two functions:

\[
X_{1}^{1}Σ^{+} = \ldots σ^4p_{Kr} \bar{σ}^4p_{Kr} | \]
\[
\check{Y}_{1}^{1}Σ^{+} = \mathcal{N} [1/\sqrt{2}] \ldots σ^4p_{Kr} \bar{σ}1s_{H}| - |\ldots\bar{σ}^4p_{Kr} σ1s_{H}| - \sqrt{2} \sum_{i}^{i} \phi_{Kr}^{i} |σ1s_{H} > \check{X}_{1}^{1}Σ^{+} ]
\]
\[
= 1/\sqrt{2} \{ |\ldotsσ^4p_{Kr} \bar{σ}1s_{H}| - |\ldots\bar{σ}^4p_{Kr} σ1s_{H}| \}
\]

where: \(σ1s_{H} = \mathcal{N} (σ1s_{H} - \Sigma \phi_{Kr}^{i} |σ1s_{H} > \phi_{Kr}^{i} )\), \(\mathcal{N}\) being a normalizing factor and \(ϕ_{Kr}^{i}\) being a Kr ground state AO.

The \(\check{Y}_{1}^{1}Σ^{+}\) state thus involves a projected AO of the type introduced by O'Malley\textsuperscript{27} in his definition of diabatic states. Therefore the states can be called projected valence bond (PVB) states\textsuperscript{24}. Considering the d/dR matrix element between the above two states one has

\[
<\check{Y}|d/dR|\check{X}> = \sqrt{2} <σ1s_{H}|d/dR|σ^4p_{Kr}>
\]
\[
= -\sqrt{2} <σ^4p_{Kr}|d/dR|σ1s_{H}>
\]
As the \( \frac{d}{dR} \) operation is carried out in keeping fixed the electron coordinates referred to the center of mass of the nuclei (CMN) and since, in addition, this origin can be considered, to a good approximation, to lie on the Kr nucleus, one gets:

\[
\langle \bar{\Phi} | \frac{d}{dR} | \bar{\Phi} \rangle = 0
\]

One then also meets with Smith's definition of diabatic states. The remaining coupling between the \( \bar{\Phi} \) and the \( \bar{\Psi} \) states is then only due to the matrix element \( \langle \bar{\Phi} | H_{\text{el}} | \bar{\Psi} \rangle \) which decreases exponentionally at large \( R \). The energy difference between the \( \langle \bar{\Phi} | H_{\text{el}} | \bar{\Phi} \rangle \) and the \( \langle \bar{\Psi} | H_{\text{el}} | \bar{\Psi} \rangle \) potential energy curves (Fig. 7) remains almost constant down to \( R \approx 4a_0 \) and it becomes equal to twice the \( \langle \bar{\Phi} | H_{\text{el}} | \bar{\Psi} \rangle \) coupling at \( R \approx 7a_0 \). The latter distance defines the charge transfer transition region. These features are those usually assumed in the charge transfer models that appeared in the literature (see e.g. ref. 26). Proceeding further and defining the \( \Sigma^+ \) and the \( \Pi \) states issuing from \( \text{H}(1s) + \text{Kr}^+(4p_5) \) in the same way as was done for \( \Sigma^+ \), it is readily seen that none of these \( \Pi \) states couples directly with the incident \( \Sigma^+ \) state.

In addition, the indirect interaction, via the doubly excited state dissociating into \( \text{H}^-(1s^2) + \text{Kr}^{++}(4p^4) \), is found to be two orders of magnitude smaller than that considered in the LCAO-SCF approach. Consequently charge transfer primarily takes place between the two \( \Sigma^+ \)-PVB diabatic states: \( \bar{\Phi} \) and \( \bar{\Psi} \).

To check the accuracy of the PVB approach, one can perform a CI calculation involving a set of singly and doubly excited PVB states and compare the results with the CI calculations involving the LCAO-SCF basis set. Very close agreement is found down to \( R \approx 4a_0 \). Below this distance, although the energy separation between the two lowest PVB + CI \( \Sigma^+ \) states is correctly reproduced, the shape of the curves is incorrect (Fig. 7). This effect is readily understood since the frozen orbitals involved in the PVB configuration state functions can hardly account for molecular distortion and polarization. These effects can, of course, be accounted for by a larger CI than was actually performed. Although such a defect should have minor consequences in the calculation of total charge transfer cross sections, it is expected to dramatically affect the interference patterns in differential cross sections, especially rainbow effects. However, as the PVB approach provides an accurate, adequate and convenient description at large \( R \) (> \( 4a_0 \)), it can be used there to treat the charge transfer process. At smaller \( R \), since the coupling between the \( \bar{\Phi} \) and \( \bar{\Psi} \) states gets much larger than their energy difference and since the PVB treatment is deficient, a more appropriate description would be based on non interacting adiabatic states (of e.g. the LCAO-SCF + CI type). The latter approach, as small \( R \), enables to properly account for interference patterns. The transformation from one description to the other is carried out at a distance \( R_D \) (Fig. 7) during the integration of the scattering equations and is very similar to the procedure described for the \( \text{He}^+ + \text{He} \) system.
Fig. 7. Scheme of the two lowest $^1\Sigma^+$ potential energy curves of the (H-Kr)$^+$ molecule ion\(^{24}\): --- SCF curves
— LCAO-SCF+CI curves
— PVB single configuration curves
• PVB + limited CI

\(R_D\) defines the distance where the basis change from the adiabatic states to the diabatic states is performed in the course of the cross section calculations\(^{23}\).

As for spin-orbit effects, which are (of course) included in our cross section calculations, they are also handled within a diabatic representation. We actually considered \(\Omega = 0^+\) states\(^{24}\). In a similar manner as that discussed for the dissociation of the states in the He$_2^+$
system, we can choose one of the three following approaches (Fig. 8):

(i) a molecular approach, at small $R$, in which the spin effects ($H_{\text{SO}}$) are dominated by the electrostatic effects. In this approach the appropriate states are the $|1^2\Sigma^+>$ and the $|3\Pi>$ states correlating with $H+$Kr+(4p$^5$).

(ii) adiabatic states which diagonalize both $H_{\text{el}}$ and $H_{\text{SO}}$ and introduce a $d/dR$ coupling.

(iii) an atomic approach, at large $R$, where spin effects dominate. The appropriate states are then constant linear combinations of the previous $|1^2\Sigma^+>$ and $|3\Pi>$ states which diagonalize $H_{\text{SO}}$.

The adiabatic representation (ii) continuously goes from case (i) to case (iii). In both cases (i) and (iii) the states are diabatic since they involve no $d/dR$ coupling (Smith's definition$^{28}$). Again as in the case of the He$^+$He collision a basis change from case (i) to case (iii) can be performed in the asymptotic region. However, since in the present system the transition occurs at large $R$, such a basis change is needless and only the representation of case (iii) is sufficient. Of course, for physical significance the basis change can be performed when actually needed.

Both the differential (Fig. 9) and total charge transfer cross sections calculated using the above method agree satisfactorily with experiment. The same procedure has been applied to the H$^+$ + Xe collision$^{31}$ and was again found to successfully account for the experimental findings$^{22}$. This method appears to be very promising and could be extended.
MOLECULAR TREATMENT OF ATOM-ATOM COLLISIONS

with great ease to other systems even if they involve lighter targets than those considered above\(^{23,32}\).

![Graph](image)

**Fig. 9.** Reduced differential cross sections for the near resonant charge transfer processes of the H\(^+\) + Kr system\(^{23}\) at \(E_L = 100\) ev.

\[
\begin{align*}
H^+ + Kr &\rightarrow H + Kr^+(2P_{3/2}) : \quad \text{--- theory, \(
\bigtriangleup\)
 experiment} \\
 &\rightarrow H + Kr^+(2P_{1/2}) : \quad \text{--- theory, \(\bullet\)}
\end{align*}
\]

**INELASTIC PROCESSES IN Li\(^+\) + HE COLLISIONS AND DIABATIC QUASI U-G CROSSINGS.**

The Li\(^+\) + He collision provides the simplest case of an asymmetric closed-shell + closed-shell interaction and has been the subject of a number of experimental works\(^{33,34,35}\). The theoretical analysis of elastic