

THE JUSTIFICATION FOR THE SEPARATION OF
ELECTRON AND NUCLEAR MOTIONS IN REACTIONS
OF ATOM-MOLECULE SYSTEMS

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Approximation methods are frequently used to examine theoretically the reactions (scattering processes with reorganization) in isolated atom-molecule systems at low energies. These methods are based on the assumption that the separation of electron and nuclear motion during the course of the whole reaction process is justifiable. This implies that, when the particles approach each other with a sufficiently small kinetic energy of their relative motion, then the initial electron wave functions, taken in the first Born-Oppenheimer approximation, are adiabatically disturbed and change directly into the electron wave functions of the final state after the separation of the particles formed in the reaction. The well-known method is used to associate the energy of the term corresponding to the common effective potential energy surface in the field of which the heavy particles move, with the electron functions depending parametrically only on the distance between the particles. In the rather more general case exchange between terms occurs (a nonadiabatic reaction) and the final number (usually not more than two) of the same comonelectron wave functions is taken into account. We shall show in this paper that such an approach, which essentially excludes the effect of the quantum mechanical character of the electron motion, cannot in fact be justified for the general case of chemical reactions and other reorganizational atom-molecule process.

Let us state the problem for the simplest example of a chemical substitution reaction



where A, B, C are different atoms and A-B and A-C are diatomic molecules.

It is not difficult to generalize the arguments below to cover more complex cases. We shall denote the initial reaction channel by the index i and the final by f . Let us introduce into the system of the center of masses the following sets of Jacobi coordinates: firstly, the set i , including the vector R_i which combines the centers of gravity of the molecule A-B and the atom C and the Jacobi coordinates inside the A-B molecule and the C atom, respectively, which comprise the vector r_i which combines the centers of gravity of the A and B atoms in A-B (with an arbitrary numeration and attribution of the electrons to the nuclei) and of the "electron" coordinates denoted by the set (ξ_i) . From the set of coordinates i we obtain the set f by substituting B \leftrightarrow C. The sets of Jacobi coordinates used were, of course, chosen nonuniquely: in particular, coordinates of the electrons can be described in each set. We shall consider the scattering process with reorganization in the normal stationary case for constant total energy $E = k_\alpha^2 / 2M_\alpha + \epsilon_\alpha$, where $\alpha = i, j$; k_α is the momentum of the relative motion along the R_α coordinate when $|R_\alpha| \rightarrow \infty$; M_α is the corresponding reduced mass; and ϵ_α is the energy of the associated states, initial and final, respectively. In solving the problem it is usually considered sufficient to find a solution of the Schrödinger equation for ψ which does not contain time. In the case of two open reaction channels this equation has the following asymptotic behavior:

$$\Psi \underset{|R_\alpha| \rightarrow \infty}{\sim} P_e \left(\delta_{\alpha_i} \exp(i\mathbf{k}_\alpha R_\alpha) + f_{\alpha_i}(\mathbf{k}_i, \mathbf{k}_f) \frac{\exp(i\mathbf{k}_\alpha R_\alpha)}{R_\alpha} \right) \varphi^\alpha(\mathbf{r}_\alpha, (\xi_\alpha)). \quad (2)$$

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The symbol P_e in Eq. (2) denotes the operation leading to antisymmetrization in the electron coordinates and spin indices, and $\varphi^\alpha(\mathbf{r}_\alpha(\xi_\alpha))$ is the product by an appropriate method of the symmetricized wave functions of the associated states of the separated molecules and the atom. * Later, with reference to the Wigner-Wietmer law we shall consider the electron spin as invariable during the reaction process and shall examine only the expansion of the complete wave function of scatter in components with a particular value of total spin. To avoid introducing new symbols we shall retain ψ from Eq. (2) for these components, understanding by P_e an operation dependent on the symmetry properties of the spin function.

If we follow literally the ideas of a method developed primarily for stationary molecule-atom states for the separation of the electron and nuclear motion (as was done in the first paper dealing with an approximation calculation), it is necessary in the case of this particular problem to expand the full Hamiltonian H into parts $H = K + H_e$, where H_e is obtained from H by a formal transfer of the nuclear masses to infinity assuming that all the remaining values are finite. Let us assume, as usual, that under the particular boundary conditions there is a complete set of functions of (ξ_α) with the necessary symmetry, being eigenfunctions from the discrete and continuous spectrum H_e , depending on $\mathbf{R}_\alpha, \mathbf{r}_\alpha$ as parameters and satisfying the condition of orthonormalization for all values of these parameters.† Let us expand the complete function $\psi(\mathbf{R}_\alpha, \mathbf{r}_\alpha, (\xi_\alpha))$ in terms of the above eigenfunctions $\Phi_k(\mathbf{R}_\alpha, \mathbf{r}_\alpha, (\xi_\alpha))$ (or their linear combinations):

$$\Psi = \sum_k \chi_k(\mathbf{R}_\alpha, \mathbf{r}_\alpha) \Phi_k(\mathbf{R}_\alpha, \mathbf{r}_\alpha; (\xi_\alpha)). \quad (3)$$

The choice of the boundary conditions for Φ_k are determined by additional considerations. In the particular problem it is advisable to introduce two sets Φ_k^i and Φ_k^f determined, respectively, in accordance with continuity by the condition

$$\Phi_k^i(\mathbf{R}_i, \mathbf{r}_i; (\xi_i)) \xrightarrow{|\mathbf{R}_i| \rightarrow \infty} \tilde{\Phi}_k^i(\mathbf{r}_i, (\xi_i)), \quad (4)$$

$$\Phi_k^f(\mathbf{R}_f, \mathbf{r}_f; (\xi_f)) \xrightarrow{|\mathbf{R}_f| \rightarrow \infty} \tilde{\Phi}_k^f(\mathbf{r}_f, (\xi_f)), \quad (4')$$

where $\tilde{\Phi}_k^\alpha[\mathbf{r}_\alpha, (\xi_\alpha)]$ are the electron wave functions forming the full set of k -electron states (including the continuous spectrum) in the channel α . In particular, we can consider that $\tilde{\Phi}_0^\alpha$ matches the electron function from which φ_α , in the Born-Oppenheimer approximation, is constructed. Each of the definitions of Eqs. (4) and (4') makes it normally possible to define the sets Φ_k^i and Φ_k^f unequivocally with accuracy, up to the simply calculated possible final degeneracy at $|\mathbf{R}_\alpha| \rightarrow \infty$. The confirmation is derived from the analytical character of the dependence of $\Phi_k^\alpha(\mathbf{R}_\alpha, \mathbf{r}_\alpha; (\xi_\alpha))$ on the $\mathbf{R}_\alpha, \mathbf{r}_\alpha$ parameters, which in turn qualitatively follows from the simple analytical dependence of H_e on these parameters. The functions of the discrete spectrum of each of the sets in Eqs. (4) and (4') may be expanded in terms of the functions of the other set. In this case, however, due to the localization of these functions as a result of the effects of saturation in different parts of space, the continuous spectrum will, in the general case, contribute to the expansions. This circumstance can clearly be explained by the character of the spectrum of the many-particle Hamiltonian H_e which is more complex than was assumed. The physical conclusion can be associated with the emergence of a supplementary degeneracy in the H_e spectrum closely associated with the exchange character of the chemical forces, i.e., with the existence of difference possibilities for the geometrical localization of electrons in the similarly arranged heavy nuclei and with the same quantum numbers.‡ It follows from the above that by using one or several of the terms in the sum, Eq. (3), for one of the Φ_k^α sets, it is impossible in the general case to construct an approximation solution ψ , satisfying the boundary conditions of Eq. (2) in both reaction channels by solving only the equation for the motion of heavy particles in the potential field of the specified electron terms. At the same time, if we restrict ourselves only to a consideration of elastic scattering or scattering with excitation but without reorganization (i.e., to the scatter channel within one reaction channel) the construction of an approximation solution by terminating the sum, Eq. (3), clearly still remains a possibility in principle.

*In this case we must use the arbitrariness, indicated above in the choice of the Jacobi coordinates.

†See, for example, [2] concerning the difficulties in the mathematical bases of these assumptions.

‡We must emphasize that in the case examined of the system containing more than two atoms it is not permissible to refer to the well known Wigner-Neumann theorem concerning the nonintersection of terms of the same symmetry.

This conclusion is closely associated with the fact that the statement of the problem of scattering with reorganization using Eq. (2) (which has been used up to the present in atom-molecule problems) is not completely correct mathematically. The latter was shown in the examination of the simpler problem of three-particle scattering [3]; Eq. (2) and the Shrödinger equation are essentially equivalent to the singular Lippman-Shvinger equations in momentum space. By avoiding the difficulties in multiparticle scattering in the way shown by L. D. Fadeev but remaining in this case within the framework of the clearer coordinate concept of the Shrödinger equation, when there are only two open reaction paths *i* and *f* we must substitute into the system

$$(K + H_e - V_i - E)\Psi_1 = -V_f\Psi_2, \quad (K + H_e - V_f - E)\Psi_2 = -V_i\Psi_1 \quad (5)$$

and make the required function ψ equal to $\psi = \psi_1 + \psi_2$. In Eq. (5) V^α is that part of the interaction terms which becomes zero when $|R_i|$ (when $\alpha = i$) or $|R_f|$ (when $\alpha = f$) tend, respectively, to infinity. The functions Ψ_1 and Ψ_2 must satisfy the boundary conditions that, as $|R_\alpha| \rightarrow \infty$, each goes over into the solution of its respective equation in (5) with zero on the right-hand side.* The preference for Eq. (5) rather than the unsplit Shrödinger equation includes the fact that in Eq. (5) the source is fairly sharply localized along all the directions in R_α and r_α coordinate space. Clearly, the splitting of the Shrödinger equation in the form of Eq. (5) becomes impossible when the expansion of Eq. (3) is used. In order to make rational use in this case of the general idea of the Born-Oppenheimer expansion we must clearly make, for example, separate expansions of the functions Ψ_1 and Ψ_2 for various initial and final electron functions. The corresponding expressions will be reported in a separate paper. In the right-hand section of Eqs. (5) the overlap integrals between the wave functions and the form factors of the initial and final states will emerge, which incidentally will justify the approach based on a distorted wave method used in considering the chemical substitution reactions in [4, 5].

In conclusion the question can be posed: whether, in general, particular cases are possible in which we can construct the approximation function of the problem of scattering using one or the final number of terms of the expansion of Eq. (3). From the above considerations we can assume on a physical basis that it is permissible only when during the reaction a true collision complex is formed which is an extension, submerged in the continuous spectrum, of the discrete spectrum of the full system. Chemically speaking this can occur only in systems in which an additive reaction can occur between A-B and C in addition to the displacement reaction, i.e., when delocalization of the valence electrons is possible throughout the A . . . B . . . C system with the formation of a chemical bond at zero (or close to zero) nuclear momentum.

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*For the sake of brevity we do not deal here with some necessary refinements associated with the antisymmetrization in the electron coordinates and also with features of long-range interaction between ions.