Interaction Potentials and Transition Probabilities

Introduction

Calculation of the angular differential cross section (for comparison with experiment or for use when experimental data are not available) requires a description of the interaction between the two colliding particles. This endeavor has kept physicists and chemists busy since the beginning of the century, the description being complicated by the fact that there are three different effects involved and, generally, many particles.

The primary effect is the coulombic force of repulsion or attraction of charged particles, which for many atomic systems is all that needs to be considered to obtain a reasonable description of the interactions. However, as there are generally a number of electrons and two nuclei involved, the net force may be rather complicated. The second effect is not so much a force, in the classical sense, as a property of electrons and nuclei at the atomic level. As any two identical atomic level particles (electrons or nuclei) cannot be distinguished by experiment, their calculated probability distributions should be identical. That is, in a theoretical description one should be able to interchange the position of any two electrons and obtain the same result for the probability amplitude to within a sign. This requirement restricts the possible distributions of electrons and is often referred to as the “exchange force.” Such a “force” also occurs when the target and incident nuclei are identical, that is, they can be interchanged without changing the character of the collision, as when a proton and a hydrogen atom collide. Lastly, the electrons and nuclei have small intrinsic magnetic fields, the magnitudes of which are proportional to a quantity called the spin of the particle, as if the fields were created by a spinning charge. These magnetic fields interact with moving charges, e.g., orbiting electrons or
colliding atoms, resulting in forces which generally, although not always, are smaller than the previous two.

To accurately describe the atomic behavior associated with the above effects, we resort to quantum mechanics. It was seen in our previous discussion (Chapter 3) that the wave motion of the heavy atomic centers could generally be treated classically, except for small-angle scattering. This is also true for very fast electrons only, as their light mass implies relatively longer wavelengths. Therefore it is useful in many instances to make the following separation: the motion of the bound electrons will be obtained from the quantum-mechanical wave equation, while the incident particle motion will be calculated classically. This separation, a special case of the Born– Oppenheimer separation, provides a starting point for understanding atomic-collision problems and has also been useful in interpreting molecular spectra.

Rather than calculate the net force on the collision centers, it is more convenient, as seen in our discussion of the deflection function, to obtain the net interaction potential. This interaction potential is the change in potential energy of the collision partners and clearly depends on the initial charge distributions of the colliding atoms. Each atom is known to have a set of states (charge distributions) characterized by a binding energy, total orbital angular momentum, and total spin. These states determine which inelastic energy losses may occur during the collision, that is, the possible final states of the colliding atoms. Associated with each pair of levels of the collision partners is an interaction potential, which makes the detailed solution of a collision problem almost impossibly complex. However, it also provides a continuous challenge to the imagination of the atomic and molecular physicist or chemist and is the source of the richness of effects associated with atomic and molecular phenomena. This complexity should not discourage the reader, as there are some obvious methods of simplification, which we will be discussing. The most obvious one, occurs when the potentials are all similar, suggesting that a common average potential can be used for all the states, an approximation we will resort to in a number of instances.

The actual interaction between collision partners is a dynamic interaction as at least one particle carries with it a cloud of electrons moving about the nucleus. Because these electrons are involved in the collision, this interaction is very different in character from the force between two bare nuclei. For two bare nuclei, the interaction at any given separation is the same whether the nuclei are standing still or moving (as long as the velocities are not near the speed of light and spin is ignored.) However, when two atoms collide, the electronic charge distributions change continuously. If the motion of the centers is slow, the electrons adjust to or follow this motion, and after the collision, essentially return to their initial configuration. This collision process is called adiabatic, as the electrons do not gain or lose
energy. That is, even though the atoms may be deflected and change kinetic energies, their initial and final internal energies are the same, and the collision is elastic. If the atomic centers approach too rapidly, the electrons on each center cannot adjust to the changes occurring in the position of the other nuclei and electrons. Because of this, abrupt changes in the charge distribution (state) may occur, similar to those occurring when light is absorbed or emitted. The effective forces between the centers obviously must differ in these two speed regions, and therefore the force is velocity dependent, making the calculations at intermediate velocities rather complicated. In the latter case, although elastic collisions may occur, there is a high probability for inelastic collisions.

Rather than treating all collision velocities by a single theoretical method, the above discussion suggests we divide collisions into rough categories. Fast collisions are those for which the relative speeds of the particles are much larger than the average speeds of the bound electrons, \( v \gg v_e \). For this case, the electron cloud can be thought of as frozen or static during the collision, except for those instances for which an abrupt change or transition occurs. The force between two atoms or an electron and an atom is, therefore, the force between static charge distributions.

At the other extreme (slow collisions, for which \( v \ll v_e \)), the electrons adjust continuously to the motion. For heavy particle interactions, when the two atomic centers are very far apart and standing still, a situation about which we can conjecture, the atoms can be thought of as distinct charge distributions. The interaction potential is simply the sum of the interactions between the charges in the two distributions and is calculated by procedures developed in classical electrostatics, as are the interactions of the frozen charge distributions discussed above. When the two atoms are brought together slowly to a new position, (Figure 4.1), their charge clouds distort, or are polarized, and the electrons redistribute themselves about the nuclei in a way determined by their initial (large \( R \)) atomic states. The net binding energy of the electrons changes in response to the distortion of the electron charge cloud, and the new charge distribution would be obtained from quantum mechanics as were the original separate, atomic charge dis-

\[ R \rightarrow \infty \]

\[ R \rightarrow 0 \]

A  B  A  B  A + B

Figure 4.1. Charge distributions on two nuclei at various internuclear separations, \( R \).
tributions. The total potential energy change of the combined system is the sum of the increased nuclear repulsion and the change in electronic binding energy. This situation is continued until $R = 0$. For two atoms the coulomb force between the nuclei becomes infinite at $R = 0$ (i.e., the potential is infinitely steep), and the electrons distribute themselves as if a single atomic center of charge $(Z_A + Z_B)e$, a united atom, were formed. Of course, the situation $R = 0$ is never reached, particularly in low-energy collisions; however, the concept of a united atom is useful theoretically for estimating the potentials at small $R$ values.

For the example in Figure 4.1, the force at large $R$ is attractive as the electron distributions are distorted to lie between the nuclei. The binding energy increases, hence the potential decreases, with decreasing $R$ until a minimum is passed and the force becomes repulsive. Such a potential with a minimum is typical for atoms in their lowest states. Adiabatic potentials can, in principle, be calculated for every orientation when molecules are involved, and such potentials are the basis for interpreting the spectra of diatomic and polyatomic molecules. Whereas fast incident electrons interact with an atom in much the same way as a bare nucleus of the same speed, slow collisions are quite different. In fact, when the incident electron speed is comparable to or less than the speeds of the bound electrons, the distinction between incident and bound electrons disappears in a close collision.

One problem with the above distinction between fast and slow collisions is that all electrons in the atoms do not have the same orbital speeds or periods. However, this can prove to be a distinct advantage. For instance, when a collision is fast with respect to the periods of the outermost electrons (outer-shell electrons), it may be adiabatic with respect to the inner-shell electrons. Therefore the inner-shell electrons return, after the collision, to their original state and only screen the interaction between the atoms. Alternatively, when considering inner-shell excitations that occur at much higher collision speeds, the outer-shell distributions can be considered frozen during the collision. For reference it is useful to remember that a proton with a speed equal to the speed of an electron in the ground-state orbit of hydrogen has an energy of about 25 keV, and, further, the orbital speed scales as $Z'$, the effective nuclear charge seen by the bound electron.

Expanding on the notion, introduced earlier, of a collision time, $\tau_c$, we define $\tau_c$ as

$$\tau_c \approx \frac{d}{v}$$

(4.1)

where $d$ is the range of the interaction, roughly the size of the colliding atoms, $d = r_A + r_B$, introduced in Chapter 2. For large $\tau_c$ the collision will be nearly adiabatic (no energy change), whereas for short $\tau_c$ inelastic effects are likely. A rough estimate of the average energy transfer can be obtained
using the collision time. The uncertainty principle states that for short times large uncertainties in energy can exist, the uncertainty being determined by

$$\Delta E \Delta \tau \geq h$$

(4.2)

where \( h \) is Planck's constant. During the collision we are clearly unable, experimentally, to ascertain the charge distribution, and therefore the energy levels are uncertain by at least

$$\Delta E \sim h/\tau_c \sim \left( \frac{h}{d} \right) v$$

(4.3)

Equation (4.3) then gives an estimate of the average inelastic energy loss expected. It is seen to be proportional to the speed, which is consistent with the above discussion; i.e., as \( v \) goes to zero, the collisions become adiabatic.

For collisions between atoms or molecules in the two limiting cases—fast and slow collisions—charge distributions, and therefore interaction potentials, can be established at each value of \( R \), the internuclear separation. In the following we obtain interaction potentials between two atomic systems, assuming that the initial charge distributions are known. Transition probabilities between the internal states of the colliding system are then estimated as a function of the speed, and inelastic cross sections are calculated from the transition probabilities. Those procedures appropriate for fast ion–atom collisions can also be used to approximate interaction potentials and transition probabilities in fast electron–atom collisions, where, in the discussion, the incident particle, A, is replaced by an electron. Slow electron collisions, however, are distinct in a number of ways, as is pointed out in the discussion. In much of the subsequent discussion we use a convenient set of units for atomic and molecular calculations appropriately called atomic units. These are defined such that \( h = 1 \), \( m_e = 1 \), and \( e = 1 \) and are described further in Appendix J.

Electrostatic Interaction between Atomic Charge Distributions

Consider two atoms, A and B, which have electronic charge distributions \( \rho_A(r_1) \) and \( \rho_B(r_2) \) and nuclei of charge \( Z_A e \) and \( Z_B e \), as shown in Figure 4.2, where \( r_1 \) and \( r_2 \) are electron position vectors about nuclei A and B respectively. The integrals, \( \int \rho_A(r_1) \, d^3r_1 = N_A \) and \( \int \rho_B(r_2) \, d^3r_2 = N_B \), give the total number of electrons on each of the atoms. For neutral atoms \( Z_A = N_A \) and \( Z_B = N_B \). The net force between the atoms is obtained from the coulombic potentials between all the constituents. For charge distributions which do not depend on \( R \), i.e., frozen charge distributions, the potential is a sum of nuclear–nuclear, electron–nuclear, and electron–
electron interactions, \( V_{\text{AB}}(R) = V_{\text{NN}} + \langle V_{\text{eN}} \rangle + \langle V_{\text{ee}} \rangle \). These have the form

\[
V_{\text{AB}}(R) = \frac{Z_A Z_B e^2}{R} - Z_A e^2 \int \frac{\rho_B(r_2) d^3r_2}{|r_2 - R|} - Z_B e^2 \int \frac{\rho_A(r_1) d^3r_1}{|r_1 + R|} + e^2 \int \int \frac{\rho_B(r_2) \rho_A(r_1) d^3r_1 d^3r_2}{|r_1 - r_2 + R|} \tag{4.4}
\]

where the brackets \( \langle \rangle \), imply an averaging of the interaction over the charge distribution. The potential given in Eq. (4.4) is for two centers of charge, A and B, but is easily generalized to include more centers when molecules collide. The cases where \( \rho_A \) and \( \rho_B \) distort will be considered shortly. The integrals in Eq. (4.4) are treated extensively in any course on electricity and magnetism, and that presentation will not be repeated here. To obtain the general nature of \( V_{\text{AB}}(R) \) for a particular pair of charge distributions, it is enough to consider the form of \( V_{\text{AB}}(R) \) for the limiting cases: \( R \) very large and very small. Also, as the differential cross section is determined primarily by the shape of the potential near the distance of closest approach, it is often not necessary to know \( V_{\text{AB}} \) accurately at all \( R \).

Defining the average radius of the atom as

\[
\bar{r} = \int r \rho(r) d^3r / N
\]

we consider the centers far apart when \( R \gg \bar{r}_1, R \gg \bar{r}_2 \). Replacing \( r_1 \) and \( r_2 \) by zero in Eq. (4.4), we see that the long-range potential becomes

\[
V_{\text{AB}}^L(R) \xrightarrow{R \to \infty} \frac{(Z_A - N_A)(Z_B - N_B)}{R} e^2 \tag{4.5}
\]

which is zero unless the particles are ions. This does not mean that the interaction potentials between neutral atoms are zero at large \( R \), but rather that they become zero faster than \( 1/R \). As \( R \to 0 \), the short-range expression from Eq. (4.4) (Problem 4.1) can be written as

\[
V_{\text{AB}}^S(R) \xrightarrow{R \to 0} \frac{Z_A Z_B e^2}{R} - \frac{Z_A Z_B e^2}{d_{\text{AB}}} \tag{4.6}
\]

where the first term is just the repulsion between the nuclei, and the second
term, a constant, is the net change in potential energy of the electrons. This
is written in terms of a characteristic length $a_{AB}$, a measure of the sizes of
the charge distributions. For a bare ion, A, colliding with a neutral atom, B,
having a hydrogenic charge distribution, we have

$$a_{AB} = a_0/Z$$

(4.7)

where $Z = Z'_B$ is the effective nuclear charge of the atom, used to determine
the charge distribution in Eq. (3.70). For two colliding atoms with identical
hydrogenic charge distributions, i.e., $Z'_A = Z'_B$, $Z$ in Eq. (4.7) is found from
Eq. (4.4) to be $Z = \frac{Z_A}{1 + Z'_B}$.

Separating the nuclei gradually from $R = 0$, we see that the nuclear repulsion
will be partially screened by the intervening cloud of electrons. As the
atomic charge density has an exponential behavior [e.g., Eq. (3.71)], it has
become customary to approximate this potential by the screened coulomb form

$$\nu_{AB}^S(R) = \frac{Z_A Z'_B}{R} e^2 \exp \left[ -R/a_{AB} \right]$$

(4.8)

which reduces to Eq. (4.6) as $R$ approaches zero. Considerable effort
has been expended in determining $a_{AB}$ for many-electron atoms. Bohr
first suggested using $a_{AB}^B = a_0(Z_{A}^{2/3} + Z_{B}^{2/3})^{-1/2}$, based on a Thomas–Fermi
charge distribution, which Lindhard later showed should be multiplied by
0.8853. Based on a similar analysis, Firsov recommended using $a_{AB}^F =
0.8853a_0(Z_{A}^{1/2} + Z_{B}^{1/2})^{-2/3}$, which differs from the Lindhard estimate by at
most 10%. For light, singly ionized, ion–atom collisions the expression
$a_{AB}^s = 2a_0(Z'_A + Z'_B)^{-1}$ has been used to obtain the screening constant. Here
$Z'_A$ and $Z'_B$ are effective charges determined from the first ionization potential
of the outer–shell electrons on A and B, e.g., $I_A = \frac{1}{2} Z_A^2 (e^2/a_0)$, where $I_B$
is the ionization energy. When such screening lengths are used, potentials in
the form of Eq. (4.8) can describe the static short-range interactions fairly
accurately.

Examining the long-range force more carefully, we note that the de-
nominators in Eq. (4.4) can be written

$$\frac{1}{|r - R|} = \frac{1}{R[1 + (r/R)^2 - 2(r/R)\cos \theta]^{1/2}}$$

(4.9)

where $\theta$ is the angle between $r$ and $R$. Expanding at large $R$, as in Eq. (3.57),
but keeping higher-order terms, one finds

$$\frac{1}{|r - R|} = \frac{1}{R} \left\{ 1 + \cos \theta \left( \frac{r}{R} \right) + \frac{1}{2} \left( \frac{r}{R} \right)^2 \left( 3 \cos^2 \theta - 1 \right) + \cdots \right\}$$

(4.10a)

We note that the angular terms are the same Legendre polynomials, Eq.
(3.15), used in the expansion of the scattering amplitude. The full expression can be written as

\[
\frac{1}{|r - R|} = \frac{1}{R} \sum_{l=0}^{\infty} \left( \frac{r}{R} \right)^l P_l (\cos \theta)
\]

(4.11)

where, at large \( R \), each successive term is smaller as \( |P_l| \leq 1 \). We noted earlier that the multipole expansion of the scattering amplitude implied that, at successive impact parameters or \( l \) values, scattering occurred from different parts of a spherically averaged potential. Here the charge distributions are not necessarily spherical and the multipole moments reflect their shapes.

If there are no electrons on one of the centers, e.g., center \( A \), the potential in Eq. (4.4) simplifies. Substituting Eq. (4.11) into the electron-nucleus interaction, we note that the long-range potential, when \( A \) is a bare nucleus or an electron, has the form

\[
V_{\text{NL}}(R) = \frac{(Z_B - N_B)Z_A e^2}{R} - Z_A e^2 \sum_{l=1}^{\infty} \frac{\overline{X_B^l}}{R^l}
\]

(4.12)

where \( \overline{X_B^l} = \int \rho_B(r_2) r_2^l P_l (\cos \theta_2) d^3 r_2 \) are the moments of the charge distribution about center \( B \), \( e \overline{X_B^l} \) is referred to as the dipole moment, often written \( \mu_B \), \( e \overline{X_B^2} \) the quadrupole moment, etc. For a spherical charge distribution all moments but the zeroth vanish. (Although the atoms may initially have spherical charge distributions, they clearly will not remain so as they approach each other, a case we will treat shortly.) Molecules, which generally do not have spherical charge distributions, may have nonzero multipole moments, with the size of \( X_B^l \) depending on the orientation of the molecule. For the interaction of \( A \) with a diatomic molecule, the orientation in question is the angle between the axis of the molecule and the vector \( R \) between \( A \) and the molecular center (Figure 4.3).

![Figure 4.3. Coordinates for bare ion, A, interacting with a diatomic molecule, BC.](image)
To complete the discussion, we return to the general case in which A has a charge distribution also. An expansion similar to that in Eq. (4.10a) is made for the electron–electron interaction in Eq. (4.4),

$$\frac{1}{|\mathbf{R} - (\mathbf{r}_2 - \mathbf{r}_1)|} = \frac{1}{R} \left\{ 1 + \frac{r_2 \cos \theta_2 - r_1 \cos \theta_1}{R} + \frac{1}{2R^2} \left[ 3(r_2 \cos \theta_2 - r_1 \cos \theta_1)^2 - |\mathbf{r}_2 - \mathbf{r}_1|^2 \right] + \cdots \right\}$$

(4.10b)

where $|\mathbf{r}_2 - \mathbf{r}_1|^2 = r_2^2 + r_1^2 - 2\mathbf{r}_1 \cdot \mathbf{r}_2$. The leading terms in the long-range potential in Eq. (4.4) can now be written, using Eqs. (4.10b) and Eq. (4.12), as

$$V_{\text{AA}}^L(R) = \frac{(Z_A - N_A)(Z_B - N_B)e^2}{R} \quad \text{ion–ion}$$

$$- (Z_A - N_A)e^2 \frac{X_B^A}{R^2} - (Z_B - N_B)e^2 \frac{X_A^B}{R^2} \quad \text{ion–dipole}$$

$$- (Z_A - N_A)e^2 \frac{X_B^A}{R^3} - (Z_B - N_B)e^2 \frac{X_A^B}{R^3} \quad \text{ion–quadrupole}$$

$$- e^2 \frac{X_B^A X_A^B}{R^3} \quad \text{dipole–dipole}$$

(4.13)

That is, the potential is the sum of the interaction of the multipole moments of the charge distributions for the two atoms, the zeroth moment being that of a point charge or ion. Here the dipole–dipole term has the form

$$e^2 X_B^A X_A^B \equiv \int \rho_A(\mathbf{r}_1) \, d^3r_1 \int \rho_B(\mathbf{r}_2) \, d^3r_2 (2x_1z_2 - x_1x_2 - y_1y_2)$$

(4.14)

where $x_1, y_1, z_1$ and $x_2, y_2, z_2$ are the components of $\mathbf{r}_1$ and $\mathbf{r}_2$ respectively. As before, the moments of spherical or spherically averaged charge distributions in Eq. (4.13) are all zero except for the ion–ion term. For neutral, molecular species the largest term in the long-range potential goes as $1/R^3$ and would depend on the relative orientation of the two molecules. Such an interaction depends on both A and B having permanent dipole moments. In the following section, we will allow the electronic charge distributions to distort. This produces additional contributions to the long- and short-range forces and is of particular interest when the charge distributions of A and B have no permanent moments.
Induced Moments: The Polarizability and the van der Waals Forces

When constructing an adiabatic potential, \( \rho_A \) and \( \rho_B \) depend on the separation \( R \), and therefore the force is not the gradient of the potential in Eq. (4.4). To obtain the appropriate potential, one calculates the binding energy of the electrons in the combined system, \( \epsilon_{AB}(R) \). Now the net change in potential energy of the system, as described in the introduction to this chapter, is

\[
V_{AB} = V_{NN} + \left[ \epsilon_{AB}(R) - \epsilon_{AB}(\infty) \right] \tag{4.15}
\]

where \( \epsilon_{AB}(\infty) \) is the initial binding energy of the electrons on the separated atoms at \( R = \infty \). For the short-range behavior at \( R = 0 \), the nuclei can be imagined to be united, as stated earlier, and the total potential energy in Eq. (4.15) becomes

\[
V_{AB}^{s} \xrightarrow{R \to 0} \frac{Z_A Z_B \epsilon^2}{R} + \left[ \epsilon_{AB}(0) - \epsilon^{A} - \epsilon^{B} \right] \tag{4.16}
\]

where \( \epsilon_{AB}(0) \), \( \epsilon^{A} \), and \( \epsilon^{B} \) are the binding energies of the combined system and the separated atoms respectively, i.e., \( \epsilon_{AB}(\infty) = \epsilon^{A} + \epsilon^{B} \). The term in brackets in Eq. (4.16) can be used now to obtain the screening constant \( a_{AB} \) in Eq. (4.6) for the adiabatic potential at small \( R \). For example, \( a_{AB} = \frac{3}{2} a_{0} \) for \( \text{H}^+ + \text{H} \), where \( \text{He}^+ \) is the united atom.

The adiabatic behavior at long range can be estimated from Eq. (4.15) or by expanding the force between distorted charge distributions in powers of \( 1/R \) and constructing a corresponding potential. For the latter case, the procedure followed is the same as that used in the previous section. Now, however, the moments of the position vectors \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) are calculated using the distorted charge distributions on each center. These charge distributions can be estimated by treating the electrons as classical oscillators, a procedure outlined at the end of Chapter 3. The interaction of a charge with a classical oscillator is treated in Appendix C. Here we use only the simple result that, if the electron oscillator is placed in a constant field, like the field of the neighboring atom, the position vector is shifted by an amount proportional to the applied field, \( \mathcal{E} \),

\[
\mathbf{r}(t) = \mathbf{r}_0(t) - \frac{e \mathcal{E}}{m_e \omega^2} \tag{4.17}
\]

In the above expression, \( \mathbf{r}_0(t) \) is the initial position vector of the electron, \( \omega \) is the frequency of the oscillator, and the nuclear position is assumed fixed. The field experienced by \( B \) due to \( A \) depends on the charge distribution on atom \( A \). This distribution is in turn distorted by the field of \( B \) and, therefore, the effective potential is obtained iteratively, being careful with orders of \( 1/R \).
In this example (i.e., using classical oscillators rather than quantum-mechanical charge distributions), the moments of the charge distribution are time averages of various powers of the position vector of the electron. For an initially spherical charge distribution, we have \( \langle r_0(t) \rangle_t = 0 \), where the brackets indicate a time average over the position vector of the oscillator. The field set up by atom A, \( \vec{\xi}_A \), induces a net dipole moment in the charge distribution of oscillator B,

\[ e\langle r_2(t) \rangle_t = -\alpha_B \vec{\xi}_A \]  

(4.18)

where, from Eq. (4.17), the quantity \( \alpha_B = e^2/m_c \omega^2 \) is the polarizability of oscillator B. The quantum-mechanical system can be thought of as made up of a collection of oscillators, each corresponding to a frequency \( \omega_k \), observed in the atomic spectrum, and each weighted by an oscillator strength \( f_k \). The sum of these oscillator strengths,

\[ \sum_k f_k = N_B \]  

(4.19)

is set equal to the number of electrons in the atom. Now the total polarizability of the atom is a weighted sum of the polarizabilities of the individual oscillators:

\[ \alpha_B = \frac{e^2}{m_c} \sum_k f_k/\omega_k^2 \]  

(4.20)

Employing our earlier notation, we write the dipole moment along \( R \) induced in B by the field of the bare ion A or electron, using Eq. (4.18), in the form

\[ (eX^1_B)_i = \alpha_B \left( \frac{Z_A e}{R^2} \right) \]  

(4.21)

Since the long-range force would have the same form whether B had an intrinsic or induced dipole moment, the potential corresponding to the dipole moment in Eq. (4.21) is easily shown to be

\[ V_{AB}^L = \frac{Z_A(Z_B - N_B)e^2}{R} - \frac{\alpha_B (Z_A e)^2}{2 R^4} + \cdots \]  

(4.22)

In taking the gradient of \( V_{AB}^L \), we now differentiate the induced moment, as well as the field. Therefore, Eq. (4.22) differs from Eq. (4.12) or Eq. (4.13) by the factor 1/2 in the ion–dipole interaction term. Equation (4.22) indicates that the largest induced term in the potential at large \( R \), due to distortions of the charge distribution, goes as \( 1/R^4 \). This can be generalized to the case where B is not spherically symmetric. One writes the one-electron dipole
moment as a permanent plus an induced moment

$$e\langle r_2(t) \rangle = e\langle r_2^o(t) \rangle + a_B \cdot \mathcal{E}_A$$

and the induced part of $V_{AB}^L$,

$$(V_{AB}^L)_i = -\frac{1}{2} \mathcal{E}_A \cdot a \cdot \mathcal{E}_A + \cdots$$  \hspace{1cm} (4.23)$$
is added to Eq. (4.12). The polarization $a$ in any direction depends on the distribution of charge in all other directions, and hence the polarizability is a tensor quantity. The reader should verify that the angular dependence of the polarizability interaction, when $B$ is a diatomic molecule, has the form

$$(V_{AB}^L)_i = -\frac{1}{2}(\cos^2 \theta \alpha_{zz} + \sin^2 \theta \alpha_{\perp}) \frac{Z_A^2 e^4}{R^4}$$

where $\alpha_{\perp}$ and $\alpha_{zz}$ are the polarizabilities perpendicular to and along the axis of the molecule, [$\alpha = (\alpha_{zz} + 2\alpha_{\perp})/2$].

From Eq. (4.20), the polarizability of an atom is seen to be inversely proportional to how tightly the electron is bound via $\omega_j$. For an atom involving a number of electrons $N_j$ in each shell, $j$, we can very roughly estimate the average polarizability in atomic units as

$$\alpha = \frac{1}{2} \sum_j N_j \omega_j$$  \hspace{1cm} \text{(4.24)}$$

where $\omega_j$ is the energy in atomic units required to remove an electron from the $j$th shell. Values of polarizabilities for a number of atoms and molecules are given in Table 4.1 and compared to this estimate, which shows the general behavior only. It is seen that the closed-shell systems, like He and Ne, have lower polarizabilities than their neighboring open-shell atoms, and the loosely bound alkali metals and larger molecules have large values of $\alpha$.

<table>
<thead>
<tr>
<th>Table 4.1. Atomic and Molecular Polarizabilities$^a$</th>
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<tbody>
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<td>Atom</td>
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<td>Na</td>
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Permanent dipole moments are also given in Table 4.1 for the non-symmetric molecules.

When center A is an atom or molecule rather than a bare ion, \( \mathcal{E}_A \) in Eq. (4.18) depends on the distribution of the electrons on A. The induced dipole moment of B then interacts with the permanent moments of A and vice versa, yielding terms of higher order in \( 1/R \). The proliferation of terms should not lead the reader to despair. Except in rare circumstances one uses only the largest one or two terms in the expansion. If, in fact, a large number of terms are required to describe the potential accurately, the expansion method is not appropriate and the interaction energies should be calculated by an alternative scheme.

Even if A and B are both neutral and spherically symmetric, a long-range interaction will occur, as their charge distributions are symmetric in an average sense only. In fact the positions of the electrons fluctuate continuously. The dipole–dipole interaction for frozen charge distributions was a result of averaging an expression involving the coordinates \( r_1 \) and \( r_2 \) over independent charge distributions in Eq. (4.14). If the charge distributions fluctuate, then the instantaneous position of \( r_2(t) \) is affected by the field \( \mathcal{E}_A \), which in turn depends on \( r_1(t) \). Therefore, the instantaneous charge distributions are not independent, producing a nonvanishing, average interaction between the induced dipoles. Note that, from the ion-induced dipole example, the instantaneous field of each oscillator is proportional to \( 1/R^3 \), indicating that the induced dipole–induced dipole interaction is of order \( 1/R^6 \),

\[ (V_{AB}^L)_d = -C_{VW}/R^6 + \cdots \]  

(4.25)

The result in Eq. (4.25) is the well-known van der Waals interaction used to describe differences in the thermodynamic behavior between a "real" gas and an ideal gas. It is the first nonvanishing term for neutral, symmetric systems and is called a dispersion interaction (hence the subscript d). That is, the interaction depends on the oscillator strengths of atoms A and B, which also determine the dispersion of light by these atoms. The van der Waals coefficient for spherical atoms has the form

\[ C_{VW} = \frac{3}{2} \frac{e^4 \hbar}{m_e^2} \sum_i \sum_j \frac{f_i^A f_i^B}{\omega_i \omega_j (\omega_i + \omega_j)} \]  

(4.26)

where the sums are over the oscillator strengths for the two atoms. The quantity \( C_{VW} \) can be estimated from the polarizabilities using the expression

\[ C_{VW} \sim \frac{1}{2} \chi_A \chi_B (\bar{I}_A^{-1} + \bar{I}_B^{-1})^{-1} \]

Here \( \bar{I}_A^{-1} \) and \( \bar{I}_B^{-1} \) are the averages of the inverse of the ionization potentials of centers A and B respectively. That is, \( \bar{I}_A^{-1} = \sum N_{Ai} / I_{Ai} \).
These long-range forces can be combined with the repulsive short-range force discussed earlier to construct semiempirical potentials for all $R$. As an example, we consider two often-used expressions. The first, for neutral symmetric systems, is the Lennard-Jones six-twelve potential [Eq. (2.62)]

$$V_{AB} \sim V_M[(R_M/R)^{12} - 2(R_M/R)^6]$$

(4.27)

Here the constants $R_M$ and $V_M$ are determined by fitting to data and/or matching with theoretical expressions. Although the repulsive part of Eq. (4.27) is not a very accurate approximation to the short-range potentials discussed earlier, the power-law form is useful, as we have seen, in estimating cross sections determined from potentials with a minimum. The constants $R_M$ and $V_M$ are the positions and depth of the minimum which may be obtained, for instance, from the molecular spectra of bound molecules. As the long-range force gradually gives way to an exponentially repulsive potential at small $R$, an expression used in ion–atom collisions is

$$V_{AB} \sim \frac{Z_A Z_B e^2}{R} \exp \left(-\frac{R}{\alpha_{AB}}\right) - \frac{\alpha_B}{2R^4} (Z_A e^2)^2 \left[1 - \exp \left(-\frac{R}{\alpha_{AB}}\right)\right]^n$$

(4.28)

where the constants $\alpha_{AB}$ and $n$ are chosen to reproduce the minimum in the potential with $n \geq 4$. There have been many attempts to describe interaction potentials with analytic forms involving a few parameters, and the reader is encouraged to look into the many excellent texts on quantum chemistry. A word of caution, however, is in order: Trying to describe a complex interaction over a broad range of internuclear separations using a couple of parameters is a hopeless procedure unless the accuracy required is not great. The best procedure, which was pointed out earlier, is to describe the potential over the small range of internuclear separations of primary importance for a particular energy regime. As a final reminder, the classical methods employed here are also limited by the fact that the constants, such as $x$ and $C_{VW}$, are in fact quantum-mechanical entities and, therefore, can only be evaluated accurately from experiment or by a wave-mechanical description of the atoms and molecules. We consider this in the following section, where the potentials found are identical in form to those above, but expressions for calculating quantities like the oscillator strength are obtained also.

**Wave-Mechanical Treatment of the Interactions**

Before proceeding further, we briefly examine the wave-mechanical treatment of the induced interactions. We remind the reader that in the Born–Oppenheimer approximation the electrons are treated separately as
moving in the field set up by the nuclei. The wave equation for electrons on fixed nuclear centers has the form

$$\left\{ -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + V_e + V_{ee} \right\} \psi^{AB} = \varepsilon^{AB}(R) \psi^{AB} \tag{4.29}$$

where the sum is over all electrons in the combined system, and $\psi^{AB}$ depends on the electron coordinates and the separation $R$. The quantity $\varepsilon^{AB}(R)$ is the total electronic binding energy of the combined system, and the term in brackets is the energy or Hamiltonian operator for the electrons, which we will write symbolically as $H_e$. After solving for $\varepsilon^{AB}(R)$ in Eq. (4.29) we can obtain the interaction potential from Eq. (4.15); that is, $V_{AB} = V_{NN} + [\varepsilon^{AB}(R) - \varepsilon^{AB}(\infty)]$.

When considering the long-range induced interaction between atoms A and B, it is useful to break $H_e$ into three parts:

$$H_e = H_A + H_B + V_{AB} \tag{4.30}$$

In Eq. (4.30), $H_A$ and $H_B$ are the Hamiltonians for the separate atoms containing the interactions between the nuclei and electrons of each atom. $V_{AB}$ is the electronic part of the interaction potential we have been discussing, prior to averaging over electronic charge distributions in Eq. (4.4). In the following, we again consider the case of a bare charge interacting with neutral atom B. For this situation, $H_e = H_B + V_{AB}^e$, and at large $R$, as $V_{AB}^e \to 0, \psi^{AB} \to \psi_j^B$. That is, the wave function of the combined system must become an atomic wave function placing the electrons on B in some state $j$. Therefore, $\psi^{AB}$ itself should assume the labels of the atomic state of B with which it correlates at large $R$, i.e., we write $\varepsilon_j^{AB}$ and $\psi_j^B$. In like manner $\varepsilon_j^{AB} \to \varepsilon_j^B$, where the atomic wave function $\psi_j^B$ is a solution of the atomic wave equation

$$H_B \psi_j^B = \varepsilon_j^B \psi_j^B \tag{4.31}$$

Treating $V_{AB}^e$ as nonzero but small at large $R$, we know that the effect of the ion A is to distort the electrons on atom B from their original configuration or state. Therefore, the wave function $\psi_j^{AB}$ becomes an admixture of the atomic states for the electrons on B,

$$\psi_j^{AB} = \sum_k c_k(R) \psi_k^B \tag{4.32}$$

where the $c_k(R)$ are coefficients that change as $R$ decreases. Clearly, when $R \to \infty$, we must require that

$$c_k(R) \to 0 \quad k \neq j \tag{4.33}$$
$$c_j(R) \to 1$$

to establish the conditions described above. Mathematically the expansion in Eq. (4.32) is equivalent to saying that the solutions of Eq. (4.31) for the
electrons on B form a complete orthogonal set of functions. That is, any perturbed or distorted wave function for the electrons can be described by a sum of the unperturbed wave functions. By the orthogonality of the solutions to the Schrödinger equation, there is no net overlap of the wave functions of \( H_B \) when integrated over all positions of the electron, much like the orthogonality of the Legendre polynomials in Eq. (3.32). This condition is expressed as

\[
\int \cdots \int \psi_j^B \ast \psi_k^B \, d^3r_1 \, d^3r_2 \cdots d^3r_{N_B} = \delta_{jk} \tag{4.34}
\]

where \( r_1, r_2, \ldots, r_{N_B} \) are the position vectors for all the electrons on B. Substituting \( \psi_j^{AB} \) as expressed in Eq. (4.32) into the Hamiltonian \( H_B + V_{eAB}^e \), and using Eq. (4.31), one obtains

\[
\sum_k c_k(R) \{ e_k^B + V_{eAB}^e \} \psi_k^B = \epsilon_j^{AB} \sum_k c_k(R) \psi_k^B
\]

An expression for any one of the coefficients, \( c_k(R) \), is obtained by multiplying by \( \psi_j^B \ast \) on the left and integrating over all the electron coordinates, as in Eq. (4.34). This procedure yields

\[
c_k(R) [\epsilon_j^{AB}(R) - \epsilon_k^B] = \sum_n c_n(R) \langle V_{eAB}^e \rangle_{kn} \tag{4.35}
\]

where the averaging implied by the brackets \( \langle \rangle \) means

\[
\langle V_{eAB}^e \rangle_{kn} = \int \cdots \int \psi_k^B \ast V_{eAB}^e \psi_n^B \, d^3r_1 \cdots d^3r_{N_B} \tag{4.36}
\]

The differential equation, Eq. (4.29), with which we started, has been reduced in Eq. (4.35) to a coupled set of linear equations which can be solved by standard matrix methods. For example, \( \epsilon_j^{AB}(R) \) is determined exactly by diagonalizing the determinant \( | \langle V_{eAB}^e \rangle_{kn} + \epsilon_k^B \delta_{kn} | \). [As there are an infinite number of states the set used in Eq. (4.32) has to be truncated.] To estimate \( \epsilon_j^{AB} \), we note that when \( \langle V_{eAB} \rangle_{kn} \) is small all the coefficients \( c_k(R) \) are small, except of course \( c_j(R) \) which remains approximately unity. Setting all the coefficients except \( c_j \) equal to zero in Eq. (4.35), we obtain a first estimate of \( \epsilon_j^{AB} \):

\[
\epsilon_j^{AB} = \epsilon_j^B + \langle V_{eAB}^e \rangle_{jj} \tag{4.37}
\]

This shows that the change in the binding energy, \( \langle V_{eAB}^e \rangle_{jj} \), is just the electronic contribution to the static potential we calculated classically! That is, replacing \( \rho_B \rightarrow | \psi_j^B |^2 \), which is the charge distribution of the initial state \( j \), we see that the total interaction potential, \( V_{AB} \approx V_{NN} + \langle V_{eAB}^e \rangle_{jj} \), has the form of Eq. (4.4) if \( A \) is a bare charge.

The first-order estimate of \( \epsilon_j^{AB} \) in Eq. (4.37) does not give any information on the effect of distortion of the wave function as the coefficients \( c_k \), \( k \neq j \), which account for the alteration of the charge cloud, are set to zero.
To account for the distortion of the charge cloud, improved estimates of the coefficients \( c_k(R) \) are needed, and we approach this using an iterative scheme to solve the set of equations in Eq. (4.35). Assuming the correction to \( \epsilon_j^{AB}(R) \) due to distortion is small, and all coefficients \( c_k \) are small except \( c_j \), we find a first estimate of the coefficients from Eq. (4.35):

\[
c_j^1(R) = -V_{kj}/(\epsilon_k - \epsilon_j) \quad k \neq j
\]

(4.38)

For convenience, we have dropped the labels B on the energies and have written \( V_{kj} = \langle V_{AB}^e \rangle_{kj} \). Using the coefficients from Eq. (4.38) in Eq. (4.35), we find an improved estimate of \( \epsilon_j^{AB} \),

\[
\epsilon_j^{AB}(R) = \epsilon_j + V_{jj} - \sum_{k \neq j} \frac{|V_{kj}|^2}{\epsilon_k - \epsilon_j}
\]

(4.39)

Continuing this procedure, we can obtain better and better estimates of the coefficients and the total binding energy. Each improvement will depend on a higher power of \( V_{AB}^e \) and therefore should decrease in importance if the interaction is weak, as it is at large \( R \).

The second term in Eq. (4.39) is the static interaction, and the third term can be related to the induced interactions discussed earlier. The latter term arises from the changes in the charge distribution, i.e., changes in the coefficients \( c_k \). The correction to the binding energy can be calculated exactly, or at large \( R \) can be estimated by expanding \( V_{AB}^e \) in powers of \( 1/R \). Substituting the expansion in Eq. (4.10a) into \( V_{kj} \) yields

\[
V_{kj} = \frac{1}{R^2} \left\langle \sum_{i=1}^{N_B} z_i \right\rangle_{kj} + \cdots
\]

Here \( z_i = r_i \cos \theta_i \), the coordinates of the electrons on B along the internuclear axis, are averaged over the wave function as in Eq. (4.36). Substituting this expression for \( V_{kj} \) into Eq. (4.39), we see that the largest term for the ion–atom interaction goes as \( 1/R^4 \), as found in the previous section. Now, however, the polarizability of B in state \( j \) can be specified and, presumably, calculated. That is, using the above expression for \( V_{kj} \), we obtain the polarizability

\[
\chi_B = 2e^2 \sum_{k \neq j} \frac{|\left\langle \sum_{i=1}^{N_B} z_i \right\rangle_{kj}|^2}{\epsilon_k - \epsilon_j}
\]

(4.40a)

Comparing Eq. (4.40a) with Eq. (4.20), we see that the oscillator strengths for an initial state \( j \), which we introduced in an \textit{ad hoc} manner before, have the form

\[
f_{kj} = \frac{2m_e}{\hbar^2} \frac{\epsilon_k - \epsilon_j}{(\epsilon_k - \epsilon_j)!} \left| \left\langle \sum_{i=1}^{N_B} z_i \right\rangle_{kj} \right|^2
\]

(4.40b)

where the frequency of the oscillator is \( \omega_{kj} = (\epsilon_k - \epsilon_j)/\hbar \). It is left as a
problem for the reader to verify that the property of the oscillator strengths \( \sum_k f_{kj} = N_B \) follows directly from Eq. (4.40b). The quantum-mechanical expression for the van der Waals coefficient, \( C_{vW} \), can be obtained by generalizing the above discussion to the case in which both atoms have charge, a problem also left for the reader, Problem 4.9.

The perturbation or iteration method above yields the static and induced interactions as separate corrections to the binding energy of the bound electrons at large \( R \). When the distortion in atom B due to center A is small, the effect is to mix in other possible charge distributions of center B. The amount of mixing is seen in Eq. (4.39) to be proportional to the square of the interaction potential and inversely proportional to the difference in binding energy between states. Therefore, states close in energy have the greatest effect on the charge distribution if the quantity \( \langle V_{AB}^x \rangle_{kj} \) is not zero, a fact we will return to below. Further, included in the sum in Eq. (4.39) are states that are solutions to Eq. (4.31) for which B is ionized, as well as the bound states of B. Such states, in fact, form a continuum of energy levels, in which case the sums in Eq. (4.39) and Eq. (4.40a) should be changed to integrals. For simplicity of notation, the sums over the bound levels and integrals over the continuum levels were indicated jointly by \( \sum_k \), as is customary.

Implicit in the perturbation approach was the fact that the corrections to \( \epsilon^A_B \) were small. At certain values of \( R \) for which either the energy spacing between two states is very small or the coupling interaction very large, the perturbation approach used above is not valid. In these regions \( \psi^A_B(R) \) often can be approximated by only two states, that is, the two closely spaced or strongly interacting states. If only two states are considered, the binding energies from Eq. (4.35) are easily solved for by diagonalizing a two-by-two determinant. This procedure yields

\[
\epsilon^A_B(R) = \frac{1}{2}(\epsilon_j + V_{jj} + \epsilon_k + V_{kk}) \\
\pm \frac{1}{2}[(\epsilon_j + V_{jj} - \epsilon_k - V_{kk})^2 + 4|V_{kj}|^2]^{1/2}
\]

(4.41)

**Figure 4.4.** Hypothetical potential energy diagrams for two strongly interacting states; \( V_{NN} + \) binding energy vs \( R \); dashed curves are the static binding energy \( (\epsilon_j + V_{jj}) \) and \( (\epsilon_k + V_{kk}) \); solid curves are the adiabatic binding energy \( \epsilon^A_B \) and \( \epsilon^A_B \) from Eq. (4.41) when \( |V_{kj}| \neq 0 \).
Figure 4.5. Correlation diagram for binding energies $\varepsilon_{\text{ab}}$ of $\text{H}^+ + \text{H}$ or the $\text{H}_2^+$ molecular ion energies and separations in atomic units.

where the plus corresponds to the upper state, and the minus the lower state, either $k$ or $j$. If the potential is again assumed to be weak, an expression for the polarizability involving only two states is recovered. Two cases for which the potential is not weak are indicated in Figure 4.4 in which are plotted hypothetical potential curves using Eq. (4.44). In the first example (a), the static estimates of the binding energies, $\varepsilon_j + V_{kk}$, are similar and in the second (b) they cross (become degenerate) at some value of $R$. In both cases, the effect of the distortion is to cause the adiabatic potential curves to separate from each other if, of course, $V_{kj}$ is nonzero. The fact that potential curves associated with states of the same symmetry, that is, those for which $V_{kj}$ is nonzero, do not cross allows one to correlate states of the separated atoms uniquely with the states of the united atom. In Figure 4.5 is given the correlation diagram for the binding energies of an $\text{H}^+ + \text{H}$ system or the $\text{H}_2^+$ molecular ion. The states at large separation are those associated with the H atom, and those at small separation are associated.
with He\(^+\). We will consider such diagrams further and will discuss the symmetries and labeling of the states below.

State Identification and Molecular Symmetries

In Appendix G the labeling and ordering of the states of atoms is reviewed. This procedure is extended here to diatomic molecules, the labeling of which will be applied to the interaction potentials between atoms. The total angular momentum, which is a well-defined quantity in a molecule, is a combination of electronic and nuclear angular momentum. In the Born–Oppenheimer approximation these can be considered separately with the nuclear angular momentum being determined by the rotational state of the diatomic, discussed in Chapter 3. For a slow collision between atoms, the corresponding quantity is the collisional angular momentum of the nuclei, \(L = mwh\). Similarly, diatomics are labeled according to their vibrational energy, which in a collision, an unbounded system, corresponds to the kinetic energy of radial motion, \(mR^2/2\). The remaining problem, therefore, is the labeling of the electronic states of the diatomic molecule.

As the electrons in a diatomic move in a field which is not spherically symmetric, the total electronic angular momentum is not a quantity that characterizes the state for all \(R\). However, the nuclear potential is symmetric with respect to rotations about the internuclear axis, hence the component of angular momentum about this axis is a well-defined quantity, i.e., one that does not depend on \(R\). Even for a single-electron diatomic molecule, there are two schemes for specifying this angular momentum and ordering the states according to energy. These schemes are based on the atomic states considered earlier. The molecular state can be imagined as being constructed by bringing two atoms together or by separating a single large atom into two nuclei. These were referred to as the separate- and united-atom limits of the molecule and were the basis for our constructing estimates for molecular potentials in the preceding sections.

In both the separate- and united-atom limit the weak electric field along the internuclear axis splits the degenerate, single-electron atomic states. This is referred to as a Stark effect. The substates of angular momentum, \(l\), separate in energy due to this field according to the \(m_l\) values, with the lowest \(|m_l|\) lying lowest in energy. In the notation of molecular spectroscopy, \(\sigma, \pi, \delta, \ldots\) are used for \(|m_l| = 0, 1, 2, \ldots\). The single-electron state is also labeled according to the atomic state of origin at either \(R = 0\) or \(R \to \infty\). For instance, a \((2p)\) state of a Li\(^+^2\) united ion having \(|m_l| = 0, 1\) can be imagined to split into \((2p\sigma)\) and \((2p\pi)\) states of a HeH\(^+^2\) diatomic ion. The corresponding notation in the separate-atom limit is: a He\(^+\)(2p) state is split by the field of a proton into a \((\sigma 2p)_{He}\) or \((\pi 2p)_{He}\) state of
HeH$^+$, where the subscript labels which center the electron was on at infinite separation.

The problem remains to correlate the states created at large $R$ with those at small $R$. As $R$ varies, the binding energy changes, according to our earlier discussion, but the $|m_l|$ label remains unchanged. The correct correlation is obtained by matching states of the same $|m_l|$ at large and small $R$ in such a way that the potentials associated with states of the same symmetry (here $|m_l|$) do not cross [viz. Eq. (4.41)]. Such a correlation diagram is shown in Figure 4.6 where the states are ordered according to their binding energy, $\varepsilon_j^{AB}(R)$. These binding energies are drawn schematically as simple lines to indicate the general nature of the change in energy as $R$

![Diagram](image)

**Figure 4.6.** Correlation diagram for an electron associated with two centers of charge $Z_A$ and $Z_B$. Vertical axis, electronic binding energy; horizontal axis, $R$. 
changes. Interaction potentials are obtained by adding the nuclear repulsion, as in Eq. (4.15).

If the nuclei are identical, then an additional symmetry is present, as the potential experienced by the electrons does not change when all the coordinates are reversed. The states themselves, therefore, can be either symmetric (gerade, g) or antisymmetric (ungerade, u) with respect to this reversal (i.e., the probability densities are unchanged). The molecular orbital energies for \( \text{He}_2^+ \) were shown in Figure 4.5. Interactions for symmetric systems are discussed in the following section.

![Correlation diagram for \( \text{He}_2^+ \) gerade states and lowest ungerade state based on orbitals in Figure 4.5, modified so orbitals of the same symmetry don’t cross. Dot-dash line: diabatic state associated with “promoted” electrons. Vertical axis, electronic binding energy; horizontal axis, \( R \).](image)

Figure 4.7. Correlation diagram for \( \text{He}_2^+ \) gerade states and lowest ungerade state based on orbitals in Figure 4.5, modified so orbitals of the same symmetry don’t cross. Dot-dash line: diabatic state associated with “promoted” electrons. Vertical axis, electronic binding energy; horizontal axis, \( R \).
A building-up principle, similar to that in Appendix G, is now used to construct multielectron states, a procedure referred to as the molecular orbital method. In this method, the total angular momentum along the axis of the diatomic molecule is a well-defined quantity, labeled $\Sigma, \Pi, \Delta, \ldots$ according to $|\sum_i (m_i)| = 0, 1, 2, \ldots$. The $\Pi, \Delta, \ldots$ states are doubly degenerate as $\sum_i (m_i)$ can be positive or negative. In addition, as the potential is symmetric with respect to reflection about any plane containing the internuclear axis, the nondegenerate $\Sigma$ states are labeled either $\Sigma^-$ or $\Sigma^+$, indicating whether the wave function changes sign or does not change sign under such a reflection. As an example, the lowest state of HeH at small $R$ is designated $(1s\sigma)^2(2s\sigma)^2 \Sigma^+$, where the superscript 2 indicates a spin doublet. The lowest state at large $R$ is $(\sigma 1s)^2_{\text{He}}(\sigma 1s)_H \Sigma^+$. As there will exist a number of states of the same symmetry, it has become customary to label the ground state by $X$ and subsequent states of higher energy by $A, B, C, \ldots$ to indicate the order. States differing in symmetry from the ground state are ordered in energy with the labels $a, b, c, \ldots$.

The correlation diagram for the lowest gerade states of the He$_2^+ 2\Sigma^+$ molecular ion is drawn schematically in Figure 4.7 from the molecular orbitals in Figure 4.5. Included also is the lowest ungerade state, which plays a role in the He$^{++}$ on He collisions. Like the atomic case, the orbital labels in a multielectron molecule give a useful, approximate picture of the molecule. As the correlation between the motions of the individual electrons is often weak, Lichten and Fano have shown that the molecular-orbital labels are quite useful in understanding transitions occurring during the collision. For instance, in a fast collision the individual electrons may follow, with high probability, the dashed curve in Figure 4.7, often referred to as a diabatic curve, which correlates with a highly excited state of the united atom and crosses many states of the same symmetry. Since there are two orbitals at large $R$ for each orbital of the same symmetry at small $R$, many such crossings will occur, a fact referred to as electron promotion. These crossings will be considered further in our discussion of transition probabilities.

The Exchange Interaction

Perturbation methods are useful for calculating the binding energy when the electronic charge distribution of one center does not overlap significantly with that of the other center. As $R$ decreases, the probability of finding an electron from B in the vicinity of A increases. In the polarizability calculation above, this is described by the more weakly bound and continuum states in the sum. These have broad charge distributions that overlap significantly with center A. In estimating the long-range interaction, the coefficient of such states is small. At very small $R$ the overlap between the electrons on A and on B is complete as the two centers merge. At
intermediate separations, when A begins to penetrate the charge cloud of B significantly, the successive corrections in the perturbation approach become significant; that is, the coefficients $\epsilon_k$, $k \neq j$, are not small. At intermediate $R$, it is therefore advantageous to include in the approximation to $\epsilon^{AB}_j$ wave functions for which the electrons are on center A.

From the energy level diagram for $H^+ + Ar$ in Figure 4.8, the state closest in energy to the ground state is the lowest state of $H + Ar^+$. Based on our previous discussion, this state will play an important role in determining the distortion of the charge cloud when the interaction matrix $V_{jk}$ between the two states is significant. In treating such a state, extra care must be taken because the wave function which places one electron on H and the rest on $Ar^+$ is not orthogonal to the wave functions for which all the electrons are on Ar. The integral of the form of Eq. (4.34) involving the ground states of $H + Ar^+$ and $Ar + H^+$, written symbolically as $\langle O_A | O_B \rangle$, is a measure of the overlap of these charge distributions. Both the overlap integral and the average interaction potential, $\langle O_A | V_{AB}^* | O_B \rangle$, between the states decrease exponentially with increasing $R$ because of the exponential nature of the atomic wave functions, e.g., Eq. (3.71). That is,

$$\langle O_A | O_B \rangle \sim \text{const} \cdot \exp\left[ -\frac{1}{2}(Z'_A + Z'_B)R/a_0 \right]$$

(4.42a)

where $Z'_A$ and $Z'_B$ are effective charges for the extra electron being on H and Ar respectively; in this example $Z'_A = 1$. Including such a state in the expansion of $\psi^{AB}_j$ would not change our previous results at large $R$, as the coefficient associated with this state would also decrease exponentially with increasing $R$. Therefore it was correct to ignore it when calculating long-range potentials even though the energy difference between the states is small. However, at intermediate $R$, when $R$ approaches the size of the atomic radii, this state will be the dominant contribution to the distortion of the charge cloud.

Figure 4.8. $ArH^+$ potentials ($V_{NN} + \epsilon^{AB}_j$) associated with lowest states of $H^+ + Ar(^1S)$ and $H(^1S) + Ar^+(^2P)$. [From approximation of R. E. Johnson, C. E. Carlson, and J. W. Boring, Chem. Phys. Lett. 16, 119 (1972).]
Approximating $\psi_j^{AB}$ by two states at intermediate $R$, which place an electron on different centers, physically implies the electron is shared by the centers. This, of course, is the nature of the covalent bond used to describe molecular structure. When the ion and atom are identical, as in the $\mathrm{H}^+ + \mathrm{H}$ system, the two states of interest, one with the electron on center A and the other with the electron on center B, have identical energies and the electron spends an equal amount of time on each center. The resulting interaction energy is referred to as an exchange interaction as two nuclei can be interchanged without affecting the physical situation. For systems like $\mathrm{H}^+ + \mathrm{Ar}$, which have ground states close in energy, the interaction at intermediate $R$ is like an exchange interaction.

In describing the interaction of a proton and a hydrogen atom, an approximate electronic wave function for the ground state at intermediate $R$ can be written as a sum of states placing the electron on center A or B,

$$\psi_0^{H^+} \approx c_A(R)\psi_0(\mathbf{r}_{1A}) + c_B(R)\psi_0(\mathbf{r}_{1B})$$  \hspace{1cm} (4.42b)

where $\psi_0$ is the ground-state atomic wave function for hydrogen. Based on the above discussion, the probability that the electron is associated with either center is the same, $|c_A|^2 = |c_B|^2$. Substituting $\psi_0^{H^+}$ into the Schrödinger equation, we obtain a set of two, coupled, linear equations. This is just the strong-coupling situation which led to Eq. (4.41), but now the atomic states are identical and the overlap is nonzero. Diagonalizing the two-by-two matrix gives $e_0^{AB}(R)$. For ground-state hydrogen two energies are obtained, as $\psi_0$ is real, these have the form

$$e_+^{AB} \simeq e_0 + \frac{\langle O_A \mid \hat{V}^e_{AB} \mid O_B \rangle + \langle O_A \mid \hat{V}^e_{AB} \mid O_B \rangle}{1 + \langle O_A \mid O_B \rangle}$$ \hspace{1cm} (4.43a)

where the plus and minus solutions correspond to $c_B = \pm c_A$. Note that when the overlap of the wave function is negligible, the correction in Eq. (4.43a) to $e_0$ is again the static interaction of Eq. (4.4) between an ion and an atom. When the overlap is not small, two states of different symmetry and different in binding energy associated with the combined molecule evolve from the two degenerate atomic states. The state lower in energy (note that $\langle V^e_{AB} \rangle$ is negative) is symmetric with respect to an interchange of A and B (i.e., $c_A = c_B$) and the upper state is antisymmetric (i.e., $c_A = -c_B$) as the sign of the wave function in Eq. (4.42b) changes on switching centers A and B. The difference in energy between these two states, $\Delta e^{AB}$, is referred to as the exchange energy. When the overlap is small but nonnegligible, the exchange energy can be written using Eq. (4.43a) as

$$\Delta e^{AB} \sim 2[\langle O_A \mid \hat{V}^e_{AB} \mid O_B \rangle - \langle O_A \mid \hat{V}^e_{AB} \mid O_A \rangle \langle O_A \mid O_B \rangle]$$ \hspace{1cm} (4.43b)

Physically it is clear that the symmetric and antisymmetric ground states of $\text{H}_2^+$ should differ in energy. In Figure 4.9 a one-dimensional plot of the
exponential-like wave functions indicates that the electron density between
the two nuclei will be larger for the symmetric wave function leading to a
lower binding energy. In fact, the electrons are excluded from the midpoint
in the antisymmetric state.

Firsov has suggested an alternate, and more accurate, method for cal-
culating $\Delta e^{AB}$, which is easily extended to larger systems. This method is
based on the flow of electrons between the two centers, yielding a general
exponential form for the exchange energy, like the overlap in Eq. (4.42a),

$$\Delta e^{AB} \sim V_0(\beta R)\exp[-\beta R]$$  \hspace{1cm} (4.43c)

where $\beta = Z'/a_0 \approx (2l)^{1/2}$; $l$ is the binding energy of the exchanged or
shared electron in atomic units. The constant $V_0$ and the power of $R$ are
determined from the atomic-orbital wave functions. Whereas the result of
the polarization of the electron cloud was to add an attractive contribution
to $V_{AB}$ at very large $R$, the effect of the exchange interaction is to split the
degenerate ground states, adding a large repulsive part to one and a large
attractive part to the other. Potential curves for the lowest two states of $H_2^+$
are given in Figure 4.10; these curves include the short-range repulsive
force. It is clear from this diagram that half the collisions of an ion with its
parent atom will involve a repulsive force, and half an attractive force, at

Figure 4.9. Schematic diagram of wave functions
for $H_2^+$. Upper: atomic states on either center.
Lower: molecular states; $g$ (gerade, symmetric),
sum of atomic states; $u$ (ungerade, antisym-
metric), difference between atomic states.

Figure 4.10. $H_2^+$ potentials associated with
$H^+ + H(1s)$ at $R \to \infty$: $V(R) = e^2/R + \epsilon^{AB}(R)$.
[From tabulations of D. R. Bates and
R. H. G. Reid, in Advances in Atomic and
Molecular Physics, Vol. 4, ed. D. R. Bates,
intermediate $R$. At very large $R$, the much weaker long-range polarization force is very nearly identical for both states. Because of the exchange interaction, the potential of the lowest state of $\text{H}_2^+$ has a form that can support bound states of the molecular ion, which are observed spectroscopically. Such states cannot be described by potentials using the polarizability as in Eq. (4.28).

In nonsymmetric systems, like the interaction of protons with argon, the interaction potentials at intermediate $R$ have a character similar to the symmetric, resonant interaction in $\text{H}_2^+$. For this nearly resonant case, an exchange-like interaction energy $\Delta e^{\text{AB}}$ splits the states, which, as we saw earlier, is generally the case for two close-lying, interacting states [e.g., Eq. (4.41)]. This energy splitting has the same general form as that for the resonant interaction in Eq. (4.43c). Now, as in Eq. (4.42a), $\beta \approx \frac{1}{2}(Z_A + Z_B)/a_0$, or $\beta \approx 1/(2)^{1/2}[(I_A^{1/2} + I_B^{1/2})]$, $I_A$ and $I_B$ being the ionization potentials in atomic units for the extra electron on center A and center B respectively. The constant and the power of $R$ are determined from the atom-orbital wave functions. This screening constant $\beta$ is often used to estimate the short-range screening length $a_{\text{AB}}$ in Eq. (4.8), i.e., $\beta^{-1} \approx a_{\text{AB}}$. In the (ArH)$^+$ system, unlike the $\text{H}_2^+$ system, the collision is either $\text{H}^+ + \text{Ar}$ or $\text{Ar}^+ + \text{H}$ and, therefore, proceeds along one potential or the whole unless a transition occurs. This will be considered shortly.

The above procedures can be extended to symmetric or nonsymmetric systems for which more than one electron is involved, for example, $\text{He}^+$ + He or $\text{H}^+ + \text{H}^-$. For interactions between identical neutral atoms, like $\text{H} + \text{H}$ and $\text{He} + \text{He}$, the nuclei again can be swapped without affecting the electronic Hamiltonian. The ground-state wave function of $\text{H}_2$ will therefore reflect this symmetry. The Heitler–London (valence-bond) method uses

$$\psi_0^{\text{AR}} \approx C_{\text{AB}}[\psi_0(r_{1A})\psi_0(r_{2B}) \pm \psi_0(r_{1B})\psi_0(r_{2A})]$$

(4.44)

where in the first term electron 1 is on A and electron 2 on B, and in the second term they are interchanged. In using Eq. (4.44) to calculate binding energies, the resulting exchange interaction, referred to as the Heitler–London interaction, again splits the degenerate levels as seen in Figure 4.11.

Whereas the two lowest states of $\text{H}_2^+$ have the same weight, in $\text{H}_2$ the relative weights of the upper and lower state are 3 to 1. This arises because the total electronic wave function must be antisymmetric with respect to the interchange of any two electrons, a basic principle of quantum mechanics (the Pauli principle) which we have not as yet invoked. The total electronic wave function is made up of the spatial wave function and the spin wave function which indicates the relative orientation of the intrinsic magnetic moments of the electrons. The spin of the electron, $S$, has a value of $\frac{1}{2}$, yielding a total intrinsic angular momentum $[S(S + 1)^{1/2}]\hbar$, e.g., Eq. (3.12).

The angular momentum has two relative orientations, "up" (+$\frac{1}{2}$) and "down" ($-\frac{1}{2}$), with spin wave functions written symbolically as $\alpha$ and $\beta$. 
respectively. The spin wave functions for two electrons are symmetric and antisymmetric products of \( \alpha \) and \( \beta \),

\[
\alpha_1 \alpha_2, \quad \beta_1 \beta_2, \quad \frac{1}{(2)^{1/2}} (\alpha_1 \beta_2 + \beta_1 \alpha_2), \quad \frac{1}{(2)^{1/2}} (\alpha_1 \beta_2 - \beta_1 \alpha_2)
\]  

(4.45)

where the subscripts indicate a particular electron. These are shown schematically in Figure 4.12. The first three, referred to as a triplet, are all symmetric with respect to interchanging 1 and 2, and all have \( S = 1 \). The other antisymmetric function, a singlet, has a net zero spin \( S = 0 \). To construct an antisymmetric wave function for the electrons, the symmetric triplet functions of Eq. (4.45) must be combined with the antisymmetric spatial wave function of Eq. (4.44), resulting in a repulsive state having three different spin orientations. The antisymmetric singlet wave function is combined with the symmetric spatial wave function to form an attractive ground state with a single spin orientation. This is the ground state of \( \text{H}_2^+ \) which is, of course, a bound state. This pair of potentials, associated with \( \text{H} + \text{H} \), therefore occurs with a three-to-one weighting (i.e., three out of four elastic collisions between two hydrogen atoms occur along a repulsive potential).

To complete the discussion of exchange effects, we note that in using the Born–Oppenheimer separation we have made an artificial distinction between the two identical charge centers in \( \text{H}_2^+ \) and \( \text{H}_2 \). The full molecular wave function should be antisymmetric with respect to an interchange of the protons (half-integer spin particles, fermions) as well as being anti-
symmetric with respect to electron exchange. For He$_2^+$ and He$_2$ the full molecular wave function should be symmetric with respect to interchange of the nuclei (bosons, integer spin particles). Such symmetry properties affect the weighting of the nuclear wave function governing the vibrational and rotational motion when combined with the nuclear spin functions. In the same way that the electronic spin functions fix the $\Sigma_a$ to $\Sigma_e$ ratio in H$_2$ at 3 to 1, the nuclear spin functions for H$_2$ fix the ratio of odd rotational states (antisymmetric) to even rotational states (symmetric) at 3 to 1. However, if one of the protons in H$_2$ is replaced by a deuteron (proton + neutron) the nuclear symmetry is broken and the even and odd rotational states are weighted equally. For our purpose, this nuclear symmetry is manifested only in low-energy and/or large-angle collisions.

The interaction potential for an incident electron is assumed to have the same form as that for a bare nucleus in a fast collision. As we saw above, however, when an electron was attached to an incident nucleus, the electronic wave function was antisymmetrized with respect to all the electrons in the incident-plus-target particle system. Similarly, the interaction between an electron and a target atom is modified by electron exchange. In fact, the incident electron and the target, e + B, can be treated as an ionized state of the B$^-$ negative ion which is fully antisymmetrized among all the electrons. As a detector cannot distinguish between a scattering of the incident electron and a capture of this electron by B with an ejection of an electron from B, this exchange effect will be manifest in slow collisions.

In the above discussion the words “exchange interaction” are seen to describe a number of different effects involving identical particles. In the following discussion, exchange interaction will refer to interactions of the type described in Eq. (4.43b) and the Heitler–London interaction. These reflect the fact that the electrons “see” identical centers of charge and, therefore, are shared equally. Charge-exchange collisions involving this interaction, as well as collisions involving identical particle interchange (e.g., protons in H$_2^+$ and electrons in e + B), will be considered shortly. In the following section we describe the calculation of transition probabilities used in inelastic-collision calculations.

**Transition Probabilities: The Impact Parameter Method**

Integrated inelastic cross sections can be calculated semiclassically using a quantum-mechanical expression for the impact parameter transition
probability $P_{AB\rightarrow J}(b)$ in Eqs. (2.24 and 2.25). These transition probabilities can also be used to describe angular differential cross sections for inelastic processes by identifying a scattering angle with each $b$. Extensive use of the impact parameter method has been made in describing inelastic energy loss in crystalline materials. Unlike single-particle experiments, in which our instruments cannot control impact parameters, multiple collisions in crystalline solids or large molecules are spatially interrelated. That is, in the short-wavelength limit, a first collision at a given impact parameter will determine the impact parameters of the subsequent collisions and, hence, the transition probabilities. In this section we approach the calculation of these transition probabilities using methods closely related to those employed above in determining the interaction potentials. Alternate approaches have been developed particularly for treating many-electron systems. Firsov, for example, describes the inelastic energy loss at each impact parameter as due to the “drag” force produced by the exchange of indistinguishable electrons between the incident and target particles during the collision. Lindhard, similarly, describes the inelastic loss via the force on the incident particle produced by the distorted electron cloud, a model we will consider further in Chapter 5. In a subsequent section of this chapter we will consider inelastic cross-section calculations via the Born approximation, a fully wave-mechanical model.

The interaction energies in the preceding sections are not only useful in calculating trajectories, but also allow us to understand inelastic transitions that occur when atoms collide. In heavy-particle collisions, the interaction potential maps the change in internal energy of the electrons and nuclei as they approach. Inelastic effects occur as transitions between two states where the energy difference of the transition during the collision is determined from the potential curves. That is, a transition can be thought of, roughly, as taking place between two potential curves, each corresponding at large $R$ to a given state of the colliding species. These transitions are usually nonradiative, implying that the energy gain or loss due to the transition comes from a slowing or speeding up of the nuclei. Quantum-mechanically, such changes in internal energy are allowed, as the nuclear kinetic energy has rather significant uncertainties during the collision [cf. Eq. (4.3)]. The net inelastic energy change after the collision is, of course, the difference between the binding energies of the final and initial states of the separated atoms.

As the electrons and nuclei must exchange energy, transitions involving small energy changes are generally favored. Because the binding energies of the electrons change during the collision, the relative spacings between the states change and, hence, the transition probabilities also vary, implying that there will be favored regions of $R$ for transitions. In Figure 4.13 three typical examples of relative spacings are shown for potential curves. In
Figure 4.13. Hypothetical potential energy diagrams for two states: $V_{NN} + e^a R$ vs $R$. Case (a): separation changes little, weak interaction between states; case (b): curve crossing between states; case (c): increasing separation at intermediate $R$ due to strong interaction between states.

example a, the spacing changes little; therefore transitions are favored at that point in the trajectory at which the interaction is strongest and the motion is slowest. This generally occurs at the distance of closest approach of the two nuclei, where the radial velocity is zero. This situation pertains to fast collisions in which the static-potential curves have roughly the same shape for each state, and the transition probabilities are small. In example b, transitions are favored where the energy spacing of the states is the smallest, that is, in the region where they cross. This produces a relatively small, abrupt change in the nuclear motion at the transition point. However, as the atoms separate, the forces on the centers are very different for the two potentials involved, resulting in a much larger gradual change in net kinetic energy of the nuclei. For case c, in which two states closely spaced at $R \rightarrow \infty$ separate significantly at smaller $R$, there again will be a most-likely transition region. At intermediate and small $R$ the significant spacing between the potentials diminishes the likelihood of a transition, and at very large $R$ the interactions are too weak to cause a transition. In the region where the curves begin to separate, the combination of the size of the interaction between the colliding particles and separation in the levels is optimal for transitions to occur. Often adiabatic curves separate, as shown in Figure 4.4a, because the states involved mix significantly. For $H^+ + \text{Ar}$ and $\text{Ar} + H^+$ ground-state curves Figure 4.8, the separation between states is a result of the strong exchange-like interaction. This interaction produces not only an optimum transition region, but also transition probabilities between the two states that may be quite large.

To calculate transition probabilities, we introduce a time dependence by assuming that the separation $R$ is a known function of time, $R(t)$, that is,
the trajectory is given. The wave equation for the electronic motion is now written

\[
\left\{ H_e [r, R(t)] - i \hbar \frac{\partial}{\partial t} \right\} \psi^{AB}(t) = 0
\]

(4.46)

where the subscript \( r \) indicates that the time derivative is taken with the electronic coordinates fixed. The solution to Eq. (4.46) can be found in the same manner that the adiabatic equation (4.29) was solved, the only difference being that the nuclei are allowed to move. As in Eq. (4.32), the wave function is expanded in terms of the states of the separated atom which, for a bare charge interacting with an atom, we write as

\[
\psi^A_B(t) = \sum_k C_{0k}(t) \psi^B_k \exp \left[ -i \frac{\varepsilon^B_k}{\hbar} t \right]
\]

(4.47)

In Eq. (4.47), the time-dependent factors discussed in Chapter 3 [Eq. (3.5)] are included. The coefficients \( C_{0k} \) are functions of time and, therefore, implicit functions of \( R \), whereas, in the time-independent problem, \( R \) was a parameter. The subscript zero now indicates the state of atom \( B \) at the start of the collision, i.e., at \( t \to \infty \),

\[
C_{00}(-\infty) = 1
\]

\[
C_{0k}(-\infty) = 0, \quad k \neq 0
\]

(4.48)

As in the time-independent case, the coefficients \( C_{0k} \) are obtained by substitution of the expansion in Eq. (4.47) into Eq. (4.46) and using the orthogonality property, Eq. (4.34), of the atomic wave functions. Now, however, the coupled linear equations are linear differential equations for each coefficient,

\[
\hbar \frac{\partial C_{0j}}{\partial t} = \sum_k C_{0k} V_{jk} \exp [i\omega_{jk} t]
\]

(4.49)

where again \( \omega_{jk} = (\varepsilon_j^B - \varepsilon_k^B)/\hbar \).

Using a perturbation method like that employed earlier, i.e., the \( V_{jk} \) are small, an approximate solution for the \( C_{0k} \) is obtained by assuming these coefficients change very little from their initial values in Eq. (4.48). With this assumption Eq. (4.49) simplifies to

\[
\hbar \frac{\partial}{\partial t} C_{0j}^1 = V_{j0} \exp [i\omega_{j0} t], \quad j \neq 0
\]

(4.50)

yielding a first-order estimate for the coefficients

\[
C_{0k}^1(\infty) = \frac{1}{i\hbar} \int_{-\infty}^{\infty} V_{k0} \exp [i\omega_{k0} t] dt
\]

(4.51)
The absolute value squared of the coefficients, \( C_{0k}(\infty) \), is the likelihood of finding the electrons in the state \( k \) after the collision. Therefore, the first-order estimate of the transition probability into a particular final state, which we label \( f \), is written

\[
P_{0 \rightarrow f}(\beta) = |C_{0f}(\infty)|^2
\]  

(4.52)

When the nuclei were moved infinitely slowly (the adiabatic problem discussed earlier), the wave function returned to the same state at large \( R \). Here, however, the electrons have a finite probability of being in a new state if the integral in Eq. (4.51), which is the fourier transform of the interaction, is nonzero. It is now explicit that the transition probability is determined, as discussed earlier, by the size of the interaction \( V_{f0} \) and the size of the inelastic energy difference \( h\omega_{f0} \). Often there are situations for which the coupling interaction is simply zero, in which case no transition occurs. This generally can be determined directly from the nature of the two states involved, in which case we say a selection rule for transitions has been found.

To evaluate the integral in Eq. (4.51) the time dependence of \( R(t) \) has to be specified. Because each state has a separate interaction potential, it is appropriate to use an average trajectory in the transition probability calculation. One such trajectory is obtained using the average instantaneous binding energy of the electrons at each time step. This reasonable but involved procedure for determining the average trajectory is generally not warranted, and at low energies is not even correct. For many collisions simple straight-line trajectories or, for close collisions, trajectories obtained from a simple screened coulomb interaction are adequate for estimating \( P_{0 \rightarrow f} \). With the straight-line trajectory (\( R^2 = b^2 + Z^2 \) and \( Z = vt \)) Eq. (4.51) becomes

\[
C_{0f}(\infty) = \frac{1}{i\hbar v} \int_{-\infty}^{\infty} V_{f0}(R) \exp \left[ \frac{i\omega_{f0}}{v} Z \right] dZ
\]  

(4.53)

The oscillating exponential in Eq. (4.53) causes cancellation in the integration. The amount of cancellation, or rapidity of the oscillations, is seen to be determined by the speed \( v \) and the energy separation, \( \hbar\omega_{f0} \). Therefore, for a given velocity, smaller changes in internal energy yield larger transition probabilities, a fact we guessed earlier. A change in velocity for a fixed \( \omega_{f0} \) affects both the oscillating exponentials and the 1/\( v \) in front of the integral. As \( v \rightarrow 0 \), the exponential term oscillates infinitely rapidly for even small increments in \( Z \), and the transition probability goes to zero in spite of the 1/\( v \) dependence in front of the integral. Such a collision is adiabatic, and no transitions between the states occur unless \( \omega_{f0} = 0 \) (i.e., the states are degenerate). For very fast collisions, as \( v \rightarrow \infty \), the exponential does not oscillate but the 1/\( v \) factor causes the coefficient to go to zero.
Here the transition probabilities are small not because of the size of the energy change, but because the collision time is short. For very fast collisions, the energy difference between the states does not play an important role and the net disturbance, \( \int x^t \psi \frac{\partial \psi}{\partial x} \, dt \), becomes small compared to \( \hbar \). The reader cannot help but notice the similarity in form between the phase shifts calculated in the impulse approximation in Eq. (3.52), which determine the elastic scattering amplitude, and the first-order transition probabilities calculated here at high energies. This similarity should not be too surprising. In wave mechanics, deflections are not the result of classical impulses to the nuclei, but rather of relative changes in phase of contributing waves. These phases can be estimated as a ratio of the classical action to the quantum-mechanical unit of action. Similarly, the coefficients in Eq. (4.53) indicate that changes in the electronic motion are due to shifts in phase, which, for fast collisions, are estimated from the ratio of the change in an electronic action, \( \int x^t \psi \frac{\partial \psi}{\partial x} \, dt \), to \( \hbar \).

As the transition probabilities go to zero both at high and low velocities, a maximum transition probability exists at some intermediate velocity for fixed \( \omega_{\psi 0} \). The discussion can be made concrete by considering an interaction of the form \( V_{\psi 0} = V_0 \exp \left[ -\beta R \right] \). From Appendix D, the first-order transition probability based on Eq. (4.53) is

\[
P_{0 \to \psi}(b) = \left( \frac{2V_0 b}{\hbar v} \right) \left( \frac{\beta}{\beta'} \right)^2 K_1(b\beta')
\]

(4.54)

where \( K_1 \) is a modified Bessel function and \( \beta' = [\beta^2 + (\omega_{\psi 0}/v)^2]^{1/2} \). \( P_{0 \to \psi} \) in Eq. (4.54) has the asymptotic forms

\[
P_{0 \to \psi}(b) \rightarrow
\begin{align*}
\text{const} \cdot v \exp \left[ -\frac{2b\omega_{\psi 0}}{v} \right], & \quad \text{as } v \rightarrow 0 \\
\text{const} \cdot \frac{1}{v^2}, & \quad \text{as } v \rightarrow \infty
\end{align*}
\]

going through a maximum located, except for very small \( b \), at \( v \sim \omega_{\psi 0}/\beta \).

The transition probabilities in Eq. (4.54) can be used to estimate the integrated inelastic cross section of Eq. (2.24),

\[
\sigma_{0 \to \psi}(v) = 2\pi \int_0^\infty P_{0 \to \psi}(b)b \, db
\]

\[
= \frac{4\pi}{3} \left( \frac{2V_0}{\hbar \omega_{\psi 0} \beta} \right)^2 \frac{(\omega_{\psi 0}/v\beta)^2}{[1 + (\omega_{\psi 0}/v\beta)^2]^3}
\]

(4.55a)

which goes through a maximum at \( v_{\text{max}} = (2)^{1/2}/\omega_{\psi 0}/\beta \). Since \( \beta^{-1} \) indicates the size of the interaction region, then \( (v\beta)^{-1} = t_\varepsilon \) is a collision time. Therefore, the location of the maximum, the so-called Massey criterion, has the form of an uncertainty principle, as discussed in the introduction to this
chapter. That is, the maximum in the cross section occurs when the allowed uncertainty in energy during the collision roughly matches the inelastic energy loss. Further, in this approximation, the sign of inelastic energy loss, $Q = \omega_{f0} \hbar$, is not important, i.e., endothermic and exothermic interactions are equally likely. The asymptotic behavior of the inelastic cross section given in Eq. (4.55a) is

$$\sigma_{i-f}^1(v) \approx \text{const} \cdot \frac{1}{v^2}, \quad \text{as } v \to \infty$$

$$\sigma_{i-f}^1(v) \approx \text{const} \cdot v^4, \quad \text{as } v \to 0$$

(4.55b)

Although the behavior at large $v$ obtained from this method is reasonably accurate for the potential chosen, the low velocity dependence is not very reliable, as seen in Figure 4.14.

In calculating the first-order transition probabilities above, we assume that the level spacing remains constant throughout the collision. To allow

![Figure 4.14](image_url)

**Figure 4.14.** Cross section for the $H^+ + H$ and $He^{2+} + H$ 1s $\rightarrow$ 2s transition calculated using the first-order transition probability in Eq. (4.53) and a better approximation, the distortion approximation in Eq. (4.56): [From D. R. Bates, *Proc. Phys. Soc (London)* 73, 227 (1959).]
for relative changes in this spacing, we recall that the diagonal interactions,
$V_{ij}$, determine the first-order improvement in the potential curves in Eqs.
(4.37). Keeping the diagonal energy terms solving Eq. (4.49), we can par-
tially account for the distortion of the electron charge cloud. The improved
coefficients, so calculated, are

$$C_{\alpha j}^{(d)}(\infty) = \frac{1}{i\hbar} \int_{-\infty}^{\infty} V_{f0} dt \exp \left[ \frac{i}{\hbar} \int_{-\infty}^{t} (\varepsilon_f + V_{ff} - \varepsilon_0 - V_{00}) dt' \right]$$  \hspace{1cm} (4.56)

when the superscript d implies the “distortion” approximation. If $V_{ff}$ and
$V_{00}$ are similar, as in Figure 4.13a, then the result in Eq. (4.53) is recovered.
When this is not the case, the distortion modifies the cross section signifi-
cantly at low energies, as seen in Figure 4.14 on the 1s $\rightarrow$ 2s transition in
hydrogen.

In heavy-particle collisions, the approximate binding energies $\varepsilon_f + V_{ff}$
and $\varepsilon_0 + V_{00}$ may become degenerate at a point $R_x$. That is, the corre-
spending potential curves cross at $R_x$, as in Figure 4.11b, in which case the
phase in the integrand of Eq. (4.56) has stationary points. By applying the
stationary phase approximation to the integral in Eq. (4.56), the reader
should verify that the transition probability becomes

$$P_{\alpha \rightarrow f}^{(d)} \approx 4 \frac{t_x}{\tau_{0f}} \sin^2 \left( \frac{1}{2\hbar} \int_{-t_x}^{t_x} (\varepsilon_f + V_{ff} - \varepsilon_0 - V_{00}) dt + \frac{\pi}{4} \right)$$  \hspace{1cm} (4.57)

where $t_x$ and $-t_x$ indicate the crossings on the incoming and outgoing
passes. Unlike the first-order estimate, the transition probability in Eq.
(4.57) has an oscillatory part. This interference term arises because the
crossing point is passed twice if $R_x > R_0$, the distance of closest approach.
In Eq. (4.57) $t_x$ is the transit time for each crossing region,

$$\tau_x = \frac{\delta R_x}{|dR/dt|_{R_x}}$$

where the extent of the interaction region, $\delta R_x$, is

$$\delta R_x = \left| 2 \left[ V_{0f} \left. \frac{d}{dR} (V_{ff} - V_{00}) \right|_{R_x} \right] \right|$$

Finally, the quantity $\tau_{0f} = [\pi |V_{0f}|/\hbar]_{R_x}^{-1}$ is a characteristic transition time.
The above expression is quite accurate when the transition region is well
separated from $R_0$ and the transition probability is small. It is usually
sufficient to use a straight-line trajectory for evaluating the phase in Eq.
(4.57), although for collisions involving significant deflections a common
average potential in the crossing region has been employed frequently. The
reader has probably noticed that the argument of the sine function in Eq.
(4.57) is the impulse approximation to the difference in the semiclassical
phase shifts of the two potential curves between the crossing points. This is just the shift in phase between a trajectory for which the transition occurs on the approach and one for which the transition occurs as the particles recede, as indicated in Figure 4.15.

When the transition probability between two states is large, the coefficients $C_{0d}(t)$ and $C_{0o}(t)$ in Eq. (4.49) cannot be estimated separately. As in the adiabatic problem, we can solve for $C_{0o}(t)$ and $C_{0f}(t)$ by integrating the two-state coupled equations. The coefficients for all other weakly coupled states can then be obtained, if necessary, using the perturbation methods. Such two-state equations have been studied extensively both for crossing and noncrossing potential curves. Solutions must be obtained numerically, but for a number of special cases analytic approximations to the transition probabilities have been found. For the case in Figures 4.13b and 4.4b in which the diabatic potentials cross each other, Landau and Zener and, independently, Stueckelberg, estimated the transition probability by solving the equations analytically in the crossing region. Defining

$$p_{0f}^{LZS} = 1 - \exp \left[ -\tau_\chi/\tau_{0f} \right]$$

(4.58)

to be the probability of a transition at each crossing, we see that the system has a probability $p_{0f}^{LZS}(1 - p_{0f}^{LZS})$ of following each of the trajectories indicated in Figure 4.15. The net probability is found to be

$$P_{0f}^{LZS} = 4p_{0f}^{LZS}(1 - p_{0f}^{LZS}) \sin^2 [\Delta \eta_{0f} + \gamma_{0f}]$$

(4.59)

where $\Delta \eta_{0f}$ is the difference in the semiclassical, radial phase shifts for the trajectories and $\gamma_{0f}$ is the additional phase factor that occurs in interference

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**Figure 4.15.** Effective potentials for the two trajectories leading to a transition when the diabatic states cross. Solid lines: adiabatic levels; dashed lines: diabatic; arrows indicate path of colliding particles.
problems [e.g., Eq. (3.51)] due to differences in signs of the contributing amplitudes. In the semiclassical approximation, the phase shift is

$$\Delta \eta_{0f}(b) = \int_{R_-}^{R_+} p^+(R)dR - \int_{R_-}^{R_+} p^-(R)dR$$  \hspace{1cm} (4.60)$$

where the plus indicates the potential determined from the electronic binding energy of the upper state and the minus the lower state in Eq. (4.41). The quantities $R_+$ and $R_-$ are the distance of closest approach for these potentials. With $\gamma_{0f} = \pi/4$, Eq. (4.59) reduces to the result in Eq. (4.57) when $V_{0f}$ is small.

For case (a) shown in Figure 4.4, in which the static potentials are similar but the coupling potential is large, direct numerical integration of the time-dependent equation indicates that a most-likely transition region exists. Approximating the lowest two states of the $H^+ + Ar$ collision by a constant energy separation to represent the static interaction potential, and an exponential coupling term to represent the exchange-like mixing of the two closely spaced states, we calculate the probability of being in the upper state as a function of time. The result is shown in Figure 4.16 for a collision with the system initially in the lower state. Transitions are seen to occur, as predicted earlier, in a well-defined region of $R$ for this case also. The effective transition region occurs at that separation for which $|V_{0f}| \approx \frac{1}{2} |\varepsilon_f + V_{ff} - \varepsilon_0 - V_{00}|$, labeled $R_x$ in Figure 4.16 and the extent of the region is,

$$\delta R_x = \frac{1}{2} \left| \frac{\varepsilon_f + V_{ff} - \varepsilon_0 - V_{00}}{dV_{0f}/dR} \right|_{R_x}$$

In these expressions, the roles of the coupling potential and the energy difference, here nearly constant, are reversed from the curve crossing case. The transition probability at the first passage is seen in Figure 4.16 to be a simple function of velocity. On exiting, however, the interference effects produce a final transition probability which oscillates significantly as a function of velocity and, of course, impact parameter.

A number of approximate expressions for the transition probability

![Figure 4.16](image-url)  \hspace{1cm} Figure 4.16. The probability of being in the excited state of $ArH^+$ (viz. Figure 4.8) during the collision. Results were obtained by numerically integrating the two-state impact-parameter equation. $R_x$ indicates the location of the transition region using the criterion $|V_{0f}| \approx \frac{1}{2} |\varepsilon_f + V_{ff} - \varepsilon_0 - V_{00}|$. [From approximation of R. E. Johnson, C. E. Carlson, and J. W. Boring, *Chem. Phys. Lett.* 16, 119 (1972)].
have been used for the case in which the static interaction potentials are nearly parallel and the coupling significant. These have the form

$$ P_{0-f}(b) = 2\overline{P}_{0f} \sin^2 \left[ \frac{1}{\hbar} \int_{-\infty}^{\infty} V_{0f} \, dt \right] $$  \hspace{1cm} (4.61a)$$

The Rosen and Zener approximation to the average transition probability is

$$ \overline{P}_{0f}^{RZ}(b) = \frac{1}{2} \left| \int_{-\infty}^{\infty} V_{0f} \exp \left[ (i/\hbar) \int_{-\infty}^{\infty} (e_f + V_{ff} - \epsilon_0 - V_{00}) \, dt \right] \right|^2 \left| \int_{-\infty}^{\infty} V_{0f} \, dt \right|^2 $$  \hspace{1cm} (4.61b)$$

At high energies and short collision times, Eqs. (4.61a) and (4.61b) reduce to the distorted wave form of $P_{0-f}$ from Eq. (4.56). Also, the argument of the sine function approximates $\Delta \eta_{0f}$ of Eq. (4.60) when the effective crossing point, $R_x$, is large. Demkov considered an exponential coupling potential, $V_{0f} = V_0 \exp(-\beta R)$, and obtained a somewhat simpler expression for $\overline{P}_{0f}$:

$$ \overline{P}_{0f}^D = \frac{1}{2} \text{sech}^2 \left\{ \frac{(\pi/2\hbar\beta)[(e_f + V_{ff} - \epsilon_0 - V_{00})/\overline{R}]}{R_x} \right\} $$  \hspace{1cm} (4.61c)$$

This expression has been used extensively to describe nonsymmetric charge exchange collisions in the intermediate velocity region and is quite accurate for $b \ll R_x$, where $R_x$ is the location of the transition region discussed above.

If the static potentials are identical and the differences in binding energies $\epsilon_0$ and $e_f$ are very small, then the average probability of a transition in Eqs. (4.61b) and (4.61c) is 1/2. This is the limiting case, discussed earlier, of symmetric resonant charge transfer, where, in fact, the initial and final states are indistinguishable and the coupling potential is the exchange energy $\Delta \epsilon^{AB}$ of Eq. (4.43). For this symmetric resonant case, the two-state equations from Eq. (4.49) can be solved exactly, and the reader should verify that the transition probability is simply

$$ P_{ct}(b) = \sin^2 \left[ \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{\Delta \epsilon^{AB}}{2} \, dt \right] $$  \hspace{1cm} (4.62)$$

Now the crossing or transition region can be thought of as occurring at infinity where the states are degenerate. The form for the symmetric resonant charge-transfer probability in Eq. (4.62) has an interesting physical interpretation. The electron can be thought of as switching between the two colliding centers during the collision, with a frequency equal to the exchange energy divided by $\hbar$. The probability of a charge transfer then depends on the collision time over the exchange period, $\tau_e/\tau_{ex}$, which is, essentially, the form of the argument of the sine function in Eq. (4.62). We also note that, for slow collisions, the symmetric resonant charge-transfer probability does not go to zero. That is, even for adiabatic collisions, the electron can end up on the other center as the nuclei are indistinguishable.
This is true only for the symmetric resonant case. For accidental resonant collisions, in which \( \omega_{f0} = 0 \), the interaction terms \( V_{ff} \) and \( V_{00} \) are not equal, causing the transition probability in Eq. (4.56) or Eq. (4.61b) to go to zero at low velocities. In Appendix I, the transition probabilities in Eqs. (4.59), (4.61a) and (4.62) are used to obtain approximate analytic expressions for inelastic cross sections.

In this discussion we have been somewhat cavalier in applying the above methods to high-energy collisions which involve charge exchange, or, for that matter, any other rearrangement. In a rearrangement collision the masses of the colliding species change during the collision; this must be accounted for in the impact parameter method. Although the mass of the electron is small, if the incident ion is moving at a speed comparable to or greater than the orbital speed of the outer electrons, the kinetic energy gain by the captured electron may be comparable to or greater than other inelastic effects. This will modify the charge-exchange probabilities and will be discussed in the following section.

An alternative approach to that given above for calculating transition probabilities in heavy-particle collisions is to begin by expanding the time-dependent wave function \( \psi^A_B(t) \) in terms of the adiabatic wave functions \( \psi^A_B(\mathbf{r}, \mathbf{R}) \), from Eq. (4.29). Substituting the wave function, with \( \mathbf{R} = \mathbf{R}(t) \),

\[
\psi^AB_0(t) = \sum_k a_{0k}(t) \psi^A_k(\mathbf{r}, \mathbf{R}) \exp \left[ - \frac{i}{\hbar} \int_{-\infty}^{t} \mathcal{E}^A_B(R) \, dt \right] \tag{4.63}
\]

into the wave equation, Eq. (4.46), we obtain the first-order estimates of \( a_{0k} \):

\[
a_{0f}(\infty) = \frac{1}{i\hbar} \int_{-\infty}^{\infty} \mathcal{V}_{f0} \exp \left[ \frac{i}{\hbar} \int_{-\infty}^{t} \left( \mathcal{E}^A_B - \mathcal{E}^A_B \right) \, dt' \right] dt \tag{4.64}
\]

where

\[
\mathcal{V}_{f0} = \int \psi^A_B^* \left( -i\hbar \frac{\partial}{\partial t_r} \right) \psi^A_0 \, d^3r
\]

The phase factor in Eq. (4.64) now depends on the differences in the adiabatic binding energies, which is simply an extension of the distorted wave result in Eq. (4.56). The coupling interaction \( \mathcal{V}_{f0} \) is very different in form, however, as it depends on the rate of change of the adiabatic states. If the collision is slow, \( \psi_0^A(t) \) remains the adiabatic wave function \( \psi^A_B(\mathbf{r}, \mathbf{R}) \) throughout the collision. Transitions are induced by the rate of change of the wave functions rather than by a potential. The time derivatives in the equation above can be written as derivatives in \( \mathbf{R} \) once the trajectories are specified, i.e., \( \partial/\partial t_r = \mathbf{v}(\partial/\partial \mathbf{R}_r) \). This expression involves changes in length, radial motion, and rotation of the internuclear axis (angular motion), referred to in the literature as radial and rotational coupling respectively. The
radial coupling clearly will not affect the angular momentum of the state. Hence, for collisions between atoms $\Sigma \rightarrow \Sigma$, $\Pi \rightarrow \Pi$, etc., transitions are allowed between the adiabatic states during the collision. The rotational coupling, however, causes transitions between states differing by one unit of angular momentum, $\Sigma \rightarrow \Pi$, $\Pi \rightarrow \Sigma$, $\Pi \rightarrow \Delta$, etc. These are referred to as the selection rules for the collisions, which are transparent in this expansion.

The static interaction potentials used in the exponent in Eq. (4.56) are a limiting case for determining the relative separation of the potential curves during the collision. The adiabatic levels, obtained by solving the full electronic Hamiltonian, $H_e$, are difficult to obtain, and the effort is often not warranted, as the wave functions are subsequently used to approximate the time-dependent electronic wave function. Other sets of wave functions and corresponding potential curves, referred to as diabatic, are often more appropriate for describing collisions at intermediate and low energies. One such set, discussed earlier, is constructed from the molecular orbitals of the quasi-molecule, in which the electron–electron interactions in Eq. (4.29) are averaged. That is, during the collision the electrons are assumed to behave independently, reacting to the field of the nuclei and the average field of the other electrons. Such states have been proven to be extremely useful, as shown by Lichten and Fano, for locating the transition regions (crossing points) of even very complex atomic systems. Although the collision time may be long, in the sense that the electrons may make a couple of orbits and the electronic cloud distorts significantly, it is often not long enough for the electrons to adjust completely to the details of the motion of all the other electrons, hence the appropriateness of the molecular orbital set of wave functions. Whereas adiabatic potential curves of the same symmetry do not cross (e.g., Figure 4.4b), these diabatic potentials do cross (e.g., Figure 4.7), and their crossing points indicate the likely transition regions. Other sets of diabatic wave functions can be imagined, with the atomic basis set, leading to the static interaction, being the appropriate set to use at high energies.

**Rearrangement Collisions: Charge Exchange**

In a rearrangement collision, one or more particles are transferred between the colliding species. If two identical particles (i.e., electrons or nuclei) are exchanged, the result is indistinguishable from collisions in which no interchange occurs. Such collisions, therefore, are not classified as rearrangement collisions, but are clearly related to the following discussion and will be considered shortly. We classify as rearrangement collisions cases in which the masses of the scattered and target particles change during the collision. We accounted for this kinematically in Chapter 2 when considering collisions of the form $A + BC \rightarrow AC + B$. Electron capture or charge
exchange is a special case for which C represents one or more electrons transferred between the particles. For heavy-particle rearrangement, the velocities change when the particle is transferred. In the present formulation these velocities occur in the time derivative, which tracks the motion of the three heavy particles,

\[ \frac{\partial}{\partial t_r} = \mathbf{v}_A \frac{\partial}{\partial \mathbf{R}_A} \bigg|_r + \mathbf{v}_B \frac{\partial}{\partial \mathbf{R}_B} \bigg|_r + \mathbf{v}_C \frac{\partial}{\partial \mathbf{R}_C} \bigg|_r \]

An electron transfer also affects the velocities slightly, but the modifications take a different form as the electron motion is described by wave mechanics. In the problem considered in the previous section, those electrons moving initially with B have, in addition to their internal motion, an overall translational velocity in the CM system, \( \mathbf{v}_B \). This motion should be described by a plane wave but was completely neglected in Eq. (4.47). When the plane-wave motion of the electrons is added to Eq. (4.47), the time-dependent wave function becomes

\[ \psi_0^{B}(t) = \sum_k C_{0k}(t) \psi_k^B(\mathbf{r}_B) \exp \left[ -i \frac{\mathbf{e}_k}{\hbar} t \right] \]

\[ \times \exp \left[ i \frac{N_B}{h} \left( m_e \mathbf{v}_B \cdot \mathbf{r}_B - \frac{m_e v_B^2}{2} t \right) \right] \quad (4.65) \]

The last factor gives for the translational motion of the electrons, e.g., Eq. (3.1), with \( \mathbf{r}_B \) measured from the CM of the system. That this is the asymptotic form for the electronic wave functions can be verified by substituting Eq. (4.65) into Eq. (4.46), where \( R \) is large, taking care with the kinetic energy derivatives for the electrons. Using Eq. (4.65) in the electronic wave equation, Eq. (4.46), we obtain the same time-dependent equations, Eq. (4.49), for the coefficients, as the additional factor is common to all the states considered. Therefore nothing changes in calculating excitation or ionization. However, when describing charge transfer, the final state of interest places at least one electron from B on A moving with CM velocity \( \mathbf{v}_A \) after the collision. The wave function for this state will involve different electron translation factors accounting for the change in momentum of the electrons.

A final, charge-exchange wave function could be described from sums of the ionized states associated with B which overlap center A. Alternatively, one can include, in the description of \( \psi_{AB}(t) \), states placing electrons on A (as in the discussion of \( H^+ + H \) and \( H^+ + Ar \)). In a manner similar to that used to estimate the exchange energy, we can approximate the time-dependent wave function by the two states, initial and final, involved in the charge exchange with the appropriate translation factors. This substitution will be left as a problem for the reader. Here we point out that the two-state time-dependent equations are exactly solvable for the sym-
metric resonant collision, yielding a transition probability for charge transfer identical in form to that in Eq. (4.62). Now, however, the exchange integrals in $\Delta e_{AB}$ [viz. Eq. (4.43b)] contain the momentum change factor $\exp(i m_e v \cdot r/\hbar)$. This translation factor has no effect when $v \to 0$; however, for fast collisions the effect of the momentum exchange is considerable. For $H^+ + H$, the overlap integrals are exactly integrable, yielding

$$
P_{et} \xrightarrow{v \to \infty} \frac{64\pi(b/a_0)^3}{(v/v_0)^2} \exp \left( - \frac{bv}{a_0 v_0} \right)
$$

(4.66a)

for charge exchange between the ground states, where $v_0$ is the velocity of the electron in the lowest Bohr orbit. Now the charge transfer cross section goes as

$$
\sigma_{et} \xrightarrow{v \to \infty} \text{const} v^{-12}
$$

(4.66b)

which differs markedly from the behavior of the excitation and ionization cross sections at high energy [e.g., Eq. (4.55b)] and decreases rapidly with increasing velocity at $v \gg v_0$.

These ideas can be applied to identical particle exchange also. That is, in a collision involving two atoms or an electron colliding with an atom, experiment cannot distinguish between the incident and target electrons after the collision. This is accounted for in the antisymmetrization of the wave function that we discussed earlier. However, the wave function describing the collision must also include the initial motion of the electrons, or the translation factors. An exchange during the collision involves a change in momentum for at least two electrons and, therefore, is also a low-velocity or large-angle effect. In resonant charge-transfer collisions (e.g., $H^+ + H$) or molecular collisions (e.g., $A + AB$) exchange of identical heavy particles must also be considered. For example, experiment cannot distinguish between a charge exchange, $H^+ + H \to H + H^+$, in which the final neutral is detected at a particular CM angle, and an elastic collision, $H^+ + H \to H^+ + H$, in which the target neutral is knocked into the same angle. In a semiclassical calculation, the two identical processes, each associated with a particular trajectory, produce interference effects in addition to those described in Chapter 3. The momentum transfer difference between these processes means that such interference effects become important only at low collision energies and/or large scattering angles. In the following section, the general nature of semiclassical, inelastic, differential cross sections is described.

**Semiclassical Approximation for Inelastic Differential Cross Sections**

The above discussion covered only transition probabilities and, hence, integrated cross sections. We postponed discussion of the semiclassical
scattering amplitude and differential cross sections for inelastic collisions until both the potential curves and transition probabilities were considered. By analogy with the results for elastic scattering in Eq. (3.35), the inelastic scattering amplitude is written

\[ f_{0 \rightarrow f}(\chi) = \frac{1}{i(k_0 k_f)} \sum_{l=0}^{\infty} (l + \frac{1}{2})P_l \{ A_{0 \rightarrow f}(l) \exp[i \eta_f^n + i \eta_0^n] - \delta_{0f} \} \]  

(4.67)

In this expression \( A_{0 \rightarrow f}(l) \) is the transition amplitude, which for simple elastic scattering is unity. The phase factor is now a sum of two phase factors associated with the initial and final states of the system, and the \( \delta_{0f} \) indicates that the subtraction at zero degrees, discussed in Chapter 3, only applies for elastic scattering. In the short-wavelength approximation the sum is again replaced by an integral, and for very long wavelengths only the \( l = 0 \) contributes. The integrated inelastic cross section for short wavelengths has the classical impact parameter form of Eq. (2.24), using Eq. (4.67) in Eq. (3.29) and the orthogonality of the Legendre polynomials:

\[ \sigma_{0 \rightarrow f} = 2\pi \int_0^\infty b \, db \, \frac{p_f}{p_0} \frac{P_{0 \rightarrow f}}{P_{0 \rightarrow f}}(b) \]  

(4.68)

Identifying \( l \) with an impact parameter, \( b \approx (l + \frac{1}{2})(k_0, k_f)^{1/2} \), we see that the transition probability is

\[ P_{0 \rightarrow f}^{(b)} = |A_{0 \rightarrow f}(b)|^2 \]  

(4.69)

and the momentum ratio, \( p_f/p_0 \), accounts for the flux change as described in Eq. (3.29). If the semiclassical approximations apply, then \( p_f \sim p_0 \), which we will assume for the remainder of this section.

Although the inelastic amplitudes \( A_{0 \rightarrow f} \) in Eq. (4.67) should be calculated directly from the full wave equation, it is clear from Eq. (4.69) that, to within a phase factor, these amplitudes can be approximated by the amplitudes \( C_{0f}(\infty) \) or \( a_{0f}(\infty) \) of Eqs. (4.47) and (4.63) calculated using the impact parameter method. When this identification is made, \( \eta_0 \) and \( \eta_f \) are the semiclassical phase shifts in Eq. (3.50b) determined from the interaction potentials of the initial and final states used in the approximation to \( \psi_0^{AB}(t) \). That is, if the adiabatic wave functions are employed, as in Eq. (4.63), these phase shifts are determined from the adiabatic binding energies. If the atomic states are used, as in Eq. (4.47), then the phase shifts are determined using the static interaction potentials, and similarly for other diabatic sets of states.

To calculate the semiclassical, angular differential cross section, the stationary-phase approximation is applied to the scattering amplitudes. Since \( A_{0 \rightarrow f} \) can be written quite generally as the product of a slowly varying function of \( b \) and an oscillatory function, the stationary phase
approximation yields

$$\sigma_{0 \rightarrow f}^{\text{sc}}(\chi) = \left| \sum_{q, \text{ all stationary points}} \left[ \tilde{P}_{0f}^{(q)} \sigma^{(q)}(\chi) \right]^{1/2} \exp \left[ i A^{(q)} / \hbar + i \gamma^{(q)} \right] \right|^2$$  \hspace{1cm} (4.70)

In Eq. (4.70) $q$ labels stationary points, each one associated with a trajectory leading to a transition $0 \rightarrow f$; $\tilde{P}_{0f}^{(q)}$ is the transition probability associated with that trajectory with a corresponding classical differential cross section $\sigma^{(q)}(\chi)$ and change in classical action $A^{(q)}$. The extra phase factor $\gamma^{(q)}$ is determined as before, viz. Eq. (3.51).

By way of understanding the result in Eq. (4.70), we refer to a couple of cases. If $C_{0f}^{(1)}$ of Eq. (4.51) is used to approximate the transition amplitudes, then $\mathcal{A}_{0 \rightarrow f}$ is a slowly varying, nonoscillatory function of $b$. Therefore, the only phase factor in the integrand of the scattering amplitude of Eq. (4.67), besides the angular factor, is $(\eta_0 + \eta_f)$, implying that the system is in the state 0 on the way in and $f$ on the way out. In essence, the transition occurs at the distance of closest approach. On the other hand, if a transition region exists at some point $R_x > R_0$, then $\mathcal{A}_{0 \rightarrow f}$ has an oscillatory factor, as expressed in Eq. (4.57), (4.59), or (4.61). When this is added to and subtracted from $(\eta_0 + \eta_f)$, two phase factors are derived, one for each of the trajectories indicated in Figure 4.15, each having a transition at $R_x$. For the curve-crossing case, $\tilde{P}_{0f}^{(q)} = p_{0f}^{LZS}(1 - p_{0f}^{LZS})$ for each trajectory, and the cross section becomes

$$\sigma_{0 \rightarrow f}^{\text{sc}}(\chi) \approx p_{0f}^{LZS}(1 - p_{0f}^{LZS}) \left( \sigma^{(1)}(\chi) + \sigma^{(2)}(\chi) - 2(\sigma^{(1)}(\chi)\sigma^{(2)}(\chi))^{1/2} \right) \cos \left[ \left( A^{(1)} - A^{(2)} / \hbar + \gamma^{(1)} - \gamma^{(2)} \right) \right]$$  \hspace{1cm} (4.71)

where 1 and 2 label quantities associated with the two trajectories in Figure 4.15. For the Rosen–Zener and Demkov transition probabilities, $\sigma_{0f}^{\text{sc}}(\chi)$ has the same form, with $p_{0f}^{LZS}(1 - p_{0f}^{LZS})$ of Eq. (4.59) being replaced by $(1/2)\tilde{P}_{0 \rightarrow f}$ of Eq. (4.61). Lastly, for symmetric resonant charge transfer, the “crossing” is at $R \rightarrow \infty$ and $p_{0f} = \frac{1}{2}$, giving

$$\sigma_{\pm}^{\text{sc}}(\chi) = \frac{1}{4} \left[ \sigma^{(g)}(\chi) + \sigma^{(u)}(\chi) \pm 2(\sigma^{(g)}(\chi)\sigma^{(u)}(\chi))^{1/2} \cos \left( \frac{A^{(g)} - A^{(u)}}{\hbar} \right) \right]$$  \hspace{1cm} (4.72)

where (g) and (u) are the labels for the symmetric and antisymmetric states (cf. Figure 4.10). The $+$ in Eq. (4.72) corresponds to elastic collisions and the $-$ to charge-transfer collisions. In Eqs. (4.71) and (4.72) a single trajectory was associated with each reaction path. Additional interference effects, such as the rainbow scattering discussed in Chapter 3, and nuclear symmetry, discussed in the preceding section, will complicate this expression somewhat as there are additional contributing trajectories. In Figure 4.17
differential cross sections for $\text{He}^+ + \text{He} \rightarrow \text{He} + \text{He}^+$ are shown in which the oscillatory pattern suggested by Eq. (4.72) is evident. At large angles in the 600 eV data, a secondary interference pattern is seen as the nuclei are identical.

At high collision energies deflections are determined primarily by the common repulsive core of the static interaction potential. At these energies the $\sigma^{\text{eff}}(\chi)$ are all roughly equivalent and the classical actions can be determined by the impulse approximation. The semiclassical cross section in Eq.
(4.10) simply reduces to

$$\sigma_{0 \rightarrow f}^{sc}(\chi) \sim P_{0 \rightarrow f} \sigma(\chi)$$  \hspace{1cm} (4.73)

where $P_{0 \rightarrow f}^{(b)}$ is the impact parameter transition probability and $\sigma(\chi)$ is a common, average differential cross section. This is a result we surmised in Chapter 2. In this form, the impact parameter transition probability is directly related to the differential cross section via a single average classical deflection function, $\chi(b)$.

The result in Eq. (4.70) can be applied to cases for which more than one crossing occurs and more than two states are involved, as long as the crossings are well separated and each trajectory is associated with a well-defined stationary point. If the number of stationary points becomes large, the scattering amplitude should be estimated from the integral form of Eq. (4.67) or via the Born approximation described in the following section.

**Transitions in the Born Approximation**

In the Born approximation described in Chapter 3, the nuclear motion was treated by wave mechanics and the interaction was assumed to be weak. The first Born result for elastic collisions in Eq. (3.60) showed that the scattering amplitude could be calculated from the initial and final plane-wave functions of the scattered particle. Generalizing this, we write the Born approximation for inelastic scattering as

$$f_{0 \rightarrow f} = \frac{m}{2\pi\hbar^2} \int \int \psi_f^*(R, r)V(R, r)\psi_0(R, r) d^3R d^3r$$  \hspace{1cm} (4.74)

The integral over $r$ in Eq. (4.74) represents integrals over the coordinates of the electrons (or other composite particles) of A and B, $R$ is the separation of A and B, and the potential is the total interaction potential before averaging over the charge distributions. If we neglect identical particle exchange, the initial and final wave functions are plane waves (for the overall motion) times the wave functions describing the initial and final atomic states in question, $\psi_f(r)$ and $\psi_0(r)$. In terms of the coupling potentials considered earlier, Eq. (4.74) can be written

$$f_{0 \rightarrow f} = \frac{m}{2\pi\hbar^2} \int \exp[-iK_f \cdot R][V_{f0}(R) + V_{NN}(R)\delta_{0f}] \exp[iK_0 \cdot R] d^3R$$  \hspace{1cm} (4.75)

where the integrations over the coordinates of the bound electrons have been performed to obtain $V_{f0}(R)$. As the scattering is not elastic, $K_f \neq K_0$;
the initial and final momenta in Eq. (4.75) are related by the inelastic energy loss
\( \hbar^2 K_f^2/2m = h^2 K_0^2/2m - Q \), where \( Q = \varepsilon_f - \varepsilon_0 = \hbar \omega_f \) and \( K_f \) is in the
direction of the detector. For elastic scattering, \( Q = 0 \), Eq. (4.75) becomes
identical to Eq. (3.59) and the interaction is the static potential.

The reader should verify (Problem 4.13) that Eq. (4.75) can be derived
from the semiclassical expression in Eq. (4.67) using Eq. (4.53) for the
transition amplitudes \( A_{0f} \). Therefore, the integrated, inelastic cross section
obtained from Eq. (4.75) is equivalent to that calculated from the impact
parameter transition probabilities if the inelastic energy loss is small
compared to the CM energy. This can be demonstrated directly, following the
method of Chapter 3, if the identification \((K_f - K_0) \cdot R = (\Delta p \cdot b)/\hbar\) is used
to define the impact parameter. Now, direct integration of the scattering
amplitude and the integrated cross section is carried out in a manner similar
to that for the elastic cross section, except that \( K_f \neq K_0 \). For \( V_{fo} \) an
exponential, e.g., Eq. (4.54), interaction, the form for the differential cross
section is similar to that in Eq. (3.64), and the integrated cross section is

\[
\sigma_{0-f} = \frac{2\pi m}{E} \left( \frac{2V_0}{\hbar^2} \right)^2 \int (\Delta p_0)^2 \left[ \frac{d(\Delta p)^2}{(\Delta p/h)^2 + \beta^2} \right]^4 \tag{4.76}
\]

In the limit \( |Q| \ll h^2 K_0^2/2m = E, \Delta p_1 \sim Q/v, \Delta p_2 \gg h\beta, \) and \( K_0 \approx K_f \),
Eq. (4.76) now yields a result identical to that in Eq. (4.55). The advantage
of starting with the Born approximation is that the angular differential
cross section is obtained directly and the form of the potential can be quite
general. When inelastic effects are studied, some caution has to be exercised
in using first-order methods. Although a transition to any state may occur
with a small probability, the sum total of such transitions might not be
small. In such cases the above expressions would need to be modified.

We briefly mention another form for the Born scattering amplitude
which has a useful physical interpretation. The Fourier transform of the
potential for an incident bare ion or electron A interacting with target atom
B can be used (see Problem 4.14) to write the scattering amplitude in Eq.
(4.75) as

\[
f^{(1)}_{0-f}(\chi) = \frac{2mZ_A e^2}{(\Delta p)^2} \left[ Z_B \delta_{f0} - \sum_{j=1}^{N_B} \int \psi_f^* \exp \left[ -i(\Delta p \cdot r_j)/h \right] \psi_0 \, d^3r \right] \tag{4.77}
\]

where \( \psi_f \) and \( \psi_0 \) are the final and initial electronic wave functions and \( d^3r \)
implies an integration over all the electronic coordinates as usual. For an
elastic collision, \( \psi_f = \psi_0 \), a result like that in Eq. (3.64) is found in which
the static charge distribution \( |\psi_0|^2 \) determines the interaction, \( V_{00} \). The first
term in Eq. (4.77) accounts for the coulomb repulsion of the nuclei and the
second term describes the impulse imparted to the electrons which may
cause a change in state. Although the interaction is split into a sum of
interactions with the individual target particles, we note the momentum transfer, $\Delta p$, involved is that for the whole target system. Momentum is not conserved separately between the incident particle and the individual particles making up the target as it was in the classical BEA discussed in Chapter 2.

The relationship between the Born and BEA approximations is very instructive and has been considered by a number of authors. Bethe pointed out that the contributions to the cross section could be understood quite easily if one considers large and small momentum transfers separately, a fact we use to simplify the calculation of the cross section. If the impulse received by the electrons is large, then after the collision the electron is very nearly a free particle not influenced by its nucleus. Now $\psi_f$ can be represented by a plane wave with momentum $\hbar k$ and the differential cross section can be written, using Eq. (4.77), as

$$d\sigma^{(1)}(k, \Delta p) \approx \frac{8\pi \hbar^3}{v^2} \left( \frac{Z_A e^2}{\Delta p} \right)^2 \sum_i N_{n_i} \rho_i(\hbar k - \Delta p) d^3k \Delta p d\Delta p \quad (4.78)$$

In the above expression, $\Delta p$ is related to the CM angle $\chi$, as before, and $\rho_i$ is the momentum distribution of the electrons in the $i$th orbital of the target atom, i.e., the absolute value squared of the Fourier transform of the orbital wave function as described at the end of Chapter 3. When the target electron is initially at rest, $\rho_i(p) = \delta(p)$, the energy transfer is $Q = \hbar^2 k^2 / 2m_e$, and we can simply integrate over $\Delta p$ and the orientation of $k$. The resulting energy-transfer cross section,

$$d\sigma^{(1)}(Q) \approx \frac{2\pi}{m_e v^2} N_{n_i} \left( \frac{Z_A e^2}{Q} \right)^2 dQ \quad (4.79)$$

is identical to the BEA cross section of Chapter 2. This is, of course, the expected result for close collisions or large momentum transfers. It should also be evident that Eq. (4.78) is equivalent to a classical BEA approximation in which an initial speed distribution for the electrons, $\rho(p)$, is included.

If the momentum transfer is small, on the other hand, the Born approximation yields quite different results. (This limit could also be approximated by considering a collision with a classical oscillator, as in Appendix C.) If $|\Delta p / \hbar| < 1$ is much less than the atomic size, then the exponential in Eq. (4.77) can be expanded. The differential cross section for a neutral target now becomes

$$d\sigma^{(1)}_{0-f}(\Delta p) \approx \frac{8\pi}{v^2} \left( \frac{Z_A e^2}{\hbar \Delta p} \right)^2 \left| \sum_{j=1}^{n_f} z_j \phi_0(\Delta p) \phi_f(\Delta p) \right|^2 d\Delta p$$

where $z_j$ is in the direction of $\Delta p$ and $\Delta p d\Delta p = \hbar^2 K_0 K_f d\cos \chi$. This is the
long-range (distance collision) dipole approximation for an inelastic collision. The dipole terms in brackets are just those used to determine the polarizability in Eq. (4.40a). The polarization interaction is, of course, an adiabatic effect in which the electronic charge cloud distorts and returns to its initial state after the collision. The result above emphasizes that, for fast collisions, the system does not always restore. The lower limit on the momentum transfer, approximately $Q/v$, is just the adiabatic cutoff postulated in Chapter 2. This quantity decreases with increasing velocity, implying that distant collisions become increasingly important at high collision energies. Therefore, the BEA approximation to the total collision cross section may be a poor approximation at high collision energies.

A useful comparison between the Born and BEA approximations can be made when considering the ionization cross section. Wave functions for ionized electrons in the vicinity of a charged particle are very much like scattered waves. They are plane-wave-like for large momentum and/or at large distances from the nuclei. Close to the nuclei they obviously are affected by the coulomb potential. Writing the energy transfer as $Q = h^2k^2/2m_e - e_0$ and changing the CM scattering angle to a momentum transfer, one can compare the cross section $d^2\sigma/dQ\,d\Delta p$ in both approximations for target hydrogen. In this comparison we use the same initial velocity distribution for Born and BEA calculations, and the exact ionization states for $\psi_f$ in Eq. (4.77). The results shown in Figure 4.18a for an incident ion differ significantly for the two approximations at small $\Delta p$ and small $Q$. The corresponding total ionization cross sections, therefore, also will differ unless the lower limits on the integration in $Q$ and $\Delta p$ are large. If, on the other hand, the incident particle is a neutral, the screening of the interaction provides a built-in cutoff at small $\Delta p$ (i.e., large $b$) and the two approximations in Figure 4.18b show considerable agreement. In the latter case the BEA cross section could be considered to be reasonably accurate.

To obtain the BEA results in Figure 4.18b, the Born cross section for the electron–hydrogen atom collision was used to represent the binary encounter between the electron and incident particle. The above comparison is based, therefore, on the premise that the cross section for an electron interacting elastically with a neutral atom is the same classically and quantum mechanically. This is a special property of the coulomb interaction (i.e., an electron colliding with an ion) but is not the case for the screened interaction, as is seen by comparing the results in Eq. (3.64) with the cross section deduced from Eq. (2.59). The following conclusion, however, holds: For incident neutrals having weak long-range interactions, the BEA is reasonably accurate.

The reader should remember that, when comparing various methods, one often forgets they are, after all, only approximate. That is, the Born and BEA methods, as well as the impact parameter and semiclassical methods,
Figure 4.18. Double differential cross section for ionization, $d^2\sigma/dQd\Delta p$, vs momentum transfer $\Delta p$ at various energy transfers, $Q$. Dashed lines, BEA; solid lines, Born, (a) H$^+$ + H; (b) H + H. This quantity is often referred to as the generalized oscillator strength for the collision. [From J. H. Harberger, R. E. Johnson, and J. W. Boring, J. Phys. B 6, 1040 (1973).]

are all approximate solutions to the collision problem and care must be taken to use each expression where appropriate. In the following chapter we discuss the results of experiments and evaluation of cross sections and related quantities using the methods developed in Chapters 2–4.
Detailed Balance

Before discussing and comparing results, we briefly consider a property of the cross sections which can be quite usefully exploited in some cases. The equations of motion, both quantum-mechanical and classical, are such that

\[ |f_{0 \rightarrow f}(x; p_0)|^2 = |f_{f \rightarrow 0}(x; p_f)|^2 \quad \text{or} \quad P_{0 \rightarrow f}(b; p_0) = P_{f \rightarrow 0}(b; p_f) \]

(4.81)

which is due to the time reversal symmetry of the collision process. Using Eq. (3.29) and Eq. (4.81) the differential cross sections for the forward and reverse reactions can be related. Further, integrating over angle [or impact parameter in Eq. (4.68)], and using Eq. (4.81), the integrated inelastic cross sections are related by

\[ p_0^2 \sigma_{0 \rightarrow f}(p_0) = p_f^2 \sigma_{f \rightarrow 0}(p_f) \]

(4.82)

In the semiclassical region \( p_0 \approx p_f \) and therefore, by Eq. (4.82), the forward and reverse reactions have the same cross section. We had stated earlier that in this region endothermic and exothermic processes behaved similarly. At low velocities, near threshold for the endothermic process, the forward and reverse reactions can differ markedly but are simply related by Eq. (4.82). This relationship is a statement of the principle of detail balance used when describing equilibrium in statistical mechanics. Based on the notions of statistical mechanics Eq. (4.82) can be extended to cases where there are a number of equivalent initial states, \( \eta_0 \), and/or final states, \( \eta_f \), (e.g., spin or angular momentum states)

\[ p_0^2 \eta_0 \sigma_{0 \rightarrow f}(p_0) = p_f^2 \eta_f \sigma_{f \rightarrow 0}(p_f) \]

(4.83)

Such a relationship allows one to determine, for instance, deexcitation cross sections from data on excitation cross sections and provides a constraint when calculating cross sections by approximate methods.

Exercises

4.1 Using the static potential of Eq. (4.4) for the interaction between A and B, obtain the expressions in Eqs. (4.5) and (4.6). Using the ground-state wave functions of H for \( \phi(r) \), obtain the result for \( a_{AB} \) in Eq. (4.7); determine \( Z \) for \( H^+ + H \) and \( H + H \).

4.2 For \( H + He \) and \( Ne + Ne \), compare graphically the screened coulomb potential of Eq. (4.8) using various screening lengths \( a_{AB}^B, a_{AB}^L, a_{AB}^S \), and \( a_{AB}^T \), all discussed below Eq. (4.8) and in Appendix H. Calculate the screened potential also from the adiabatic expression for \( a_{AB} \) using Eq. (4.16).
4.3. Consider a simple ionic-bonded molecule (B⁺C⁻) interacting with a charged particle A⁺. If the equilibrium internuclear separation of the molecule is 2.5\( a_0 \) and the binding force is characterized by a frequency \( \nu_0 = 10^{12} \text{ sec}^{-1} \), compare the ion–dipole and ion–induced dipole potentials graphically.

4.4. Using the ground-state hydrogenic wave function, calculate \( V_{NN} + V_{00} \), the static interaction, for H⁺ + H.

4.5. For H⁺ + H, calculate \( \langle O_A | O_B \rangle \) and \( \langle O_A | V_{AB}^* | O_B \rangle \) using the ground-state hydrogen wave function. Show that they depend exponentially on \( R \) at large \( R \). Evaluate and plot \( V_{NN} + \epsilon_{AB}^* \) in Eq. (4.43a). [Note: The integration can be carried out by expansion, as in Eq. (4.10a), or by using the prolate spheroidal coordinates, \( \zeta = (r_{1A} + r_{1B})/2R \), \( \eta = (r_{1A} - r_{1B})/2R \) and \( \phi \).] Compare to the polarizability interaction with \( \alpha_H = 4.5a_0^3 \) and to the results in Figure 4.10.

4.6. Consider a hydrogen atom in a small electric field (e.g., that produced by an approaching atom). Use the perturbation method employed in solving Eq. (4.35) to obtain the splitting of the degenerate \( m_l \) values. Employ the wave functions of Chapter 3.

4.7. For the system A⁺⁺ + B → A⁺ + B⁺, a series of curve crossings occurs. The potential \( V_{00} \) for A⁺⁺ + B goes as \( V_{00} \sim -(z^2/2)(Z^2/R^6) \), with \( Z = 2 \), whereas the potential \( V_{ff} \) for A⁺ + B⁺ goes as \( V_{ff} \sim 1/R \), in atomic units. For He⁺⁺ + Ne, plot the potentials and find the curve crossings for the first few states of He⁺⁺: \( x_{Ne} \simeq 13a_0 \) and \( I_{Ne} = 21.56 \text{ eV} \).

4.8. Given the expression for the oscillator strength in Eq. (4.40b), show that \( \sum_k f_{k0} = N_B \). Use the fact that \( (\epsilon_k - \epsilon_0)(\sum \delta_z z_i)_{k0} = \langle [H_B, \sum \delta_z z_i] \rangle_{k0} \), invoking Eq. (4.31), where \([H, z] \) means \( Hz - zH \).

4.9. For H + H, use London’s method to evaluate the coefficient \( C_{\psi\psi} \) from the first-order corrections to the wave functions for \( \psi_{AB} \). This is obtained by writing \( \psi_{AB}(R) = \sum_i \sum_j C_{ij}(R) \psi_i^A \psi_j^B \) and substituting into \( H_{A} = H_A + H_B + V_{AB} \), a procedure similar to that used to obtain the set of equations in Eq. (4.35). Finally, employ the expansion for \( V_{AB}^* \) from Eq. (4.10b).

4.10. Calculate the transition probability in Eq. (4.53) if \( V_{00}(R) \) is a power law (Appendix D), \( V_{0f} \propto R^{-n} \). What are the asymptotic limits to the cross section \( \sigma_{0f} \) at high and low \( \nu \)?

4.11. Use the stationary-phase approximation of Appendix F to obtain Eq. (4.57) from Eq. (4.56).

4.12. Solve the two-state, time-dependent equations for the transition probabilities in a symmetric resonant collision. Verify Eq. (4.62) for the charge-transfer probability and obtain the high-energy limit for the H⁺ + H collision using the wave functions in Eq. (3.71).

4.13. Use the semiclassical scattering amplitude in Eq. (4.67) to derive the Born expression in Eq. (4.75) when the phase shifts are small. Assume \( \delta_{0f} = \delta_{1f} = 0 \) in Eq. (4.53) and define the impact parameter from \( (K_f - K_0) \cdot R = \Delta p \cdot b/\hbar \).

4.14. Evaluate the fourier transform of the coulomb potential, \( \int d^3R \exp[iK \cdot R]/R \). Use this to write the scattering amplitudes in Eq. (4.75) in the form of Eq. (4.77), when the incident particle is a bare nucleus.

4.15. Verify that Eq. (4.76) is equivalent to Eq. (4.55a) if \( |Q| \ll E \).
Suggested Reading

As in Chapters 2 and 3, most of this material is contained in texts on atomic and molecular collisions, quantum mechanics, or quantum chemistry. Specific examples are given below; references for transitions, inelastic cross sections and charge exchange overlap considerably and the divisions of titles are somewhat arbitrary.

Intermolecular Potentials


Exchange Energy

O. Firsov, Zh. Eksp. Teor. Fiz. 21, 1001 (1951), and texts above.


Molecular Orbitals and Correlation Diagrams


Stationary Perturbation Theory


Time-Dependent Perturbation Theory and Impact-Parameter Transition Probabilities


Interaction Potentials and Transition Probabilities


**Born Approximation: Transitions**


**Semiclassical, Inelastic Differential Cross Sections**


**Charge Exchange**


