

## Collision Systems

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### Abstract

Various approximations which are possible for the theoretical description of colliding ion-atom systems are reviewed. With the emphasis on relativistic influences, a few comparisons of experimental results with relativistic calculations are made.

### 1. Introduction

When two many-electron atoms or ions collide with each other, a large number of processes can occur: inner- and outer-shell ionization via one- or more step processes followed by separated atom and molecular x-rays and/or Auger transitions and their cascades. The cross sections of each of these processes strongly depend on the impact energy as well as the charges of the two nuclei and the number of electrons involved. From a theoretical viewpoint such systems are many-body problems par excellence.

In classical quantum chemistry, such problems (where the nuclear charges and the number of electrons involved are very low as are the impact energies) are treated. However, recent developments in accelerators made the whole range of energies and nuclear charges (up to  $U - U$ ) available for experiments, which means that relativistic effects have to be included. Since *ab initio* fully quantum-mechanical calculations are not available, it is important to distinguish between various possible approximations.

Two important quantities in a collision process are the distance of closest approach which (for a Rutherford trajectory) is  $R_{\min} = 2 \cdot Z_1 \cdot Z_2 \cdot e^2 / M \cdot v_I^2$  and the de Broglie wavelength  $\lambda = \hbar / M \cdot v_I$ . Their quotient is the Sommerfeld parameter  $\eta = R_{\min} / 2\lambda = Z \cdot Z_2 \cdot e^2 / \hbar \cdot v_I$ . If  $\eta \ll 1$ , a quantum mechanical description of nuclear motion is necessary and if  $\eta \gg 1$ , a classical description of the nuclear motion is appropriate. In addition, the adiabatic parameter  $\tau = v_I^2 / v_{el}^2$ , where  $v_{el}$  is the electron velocity, is often used.  $\tau \ll 1$  is called adiabatic and  $\tau \gg 1$  is called sudden or nonadiabatic.

The aim of this paper is to review from a general viewpoint the various approximations which are being used in the theoretical treatment of collision problems [1] as well as the influence of relativity for some very heavy systems. A brief comparison of a few experiments with new calculations is made.

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## 2. Quantum-Mechanical Treatment of Nuclear Motion

In this very general case the time-independent Schrödinger (or Dirac) equation has to be solved

$$(H - E)\Psi(\mathbf{x}, \mathbf{R}) = 0, \quad (1)$$

where  $H$  is the full Hamiltonian of the system,  $\mathbf{x}$  is the electronic coordinates, and  $\mathbf{R}$  is the internuclear distance. If we use  $H = -\nabla_R^2/2M + H_e + V$  and know the solution of

$$H_e\psi_n(\mathbf{x}, \mathbf{R}) = E_n(R)\psi_n(\mathbf{x}, \mathbf{R}), \quad (2)$$

we can use  $\psi_n$  as basis functions. With

$$\Psi(\mathbf{x}, \mathbf{R}) = \sum_n F_n(\mathbf{R})\psi_n(\mathbf{x}, \mathbf{R}), \quad (3)$$

we get a set of coupled differential equations

$$\begin{aligned} [\nabla_R^2 + k_n^2]F_n(R) &= 2M \sum_m \langle \psi_n | V | \psi_m \rangle F_m(\mathbf{R}) \\ &\quad - 2 \sum_{m \neq n} \langle \psi_n | \nabla_R | \psi_m \rangle F_m(\mathbf{R}) \\ &\quad - \sum_{m \neq n} \langle \psi_n | \nabla_R^2 + k_n^2 | \psi_m \rangle F_m(\mathbf{R}), \end{aligned} \quad (4)$$

with  $k_n^2 = 2M[E - E_n(R)]$ .

Asymptotically the right-hand side goes to zero. For the incident channel at  $t \rightarrow \infty$  we have

$$F_0(\mathbf{R}) \sim \exp(i\mathbf{k}_0\mathbf{R}) + \frac{1}{R} \exp(ik_0R)f_0(\vartheta, \varphi), \quad (5)$$

and the other channels behave like

$$F_n(R) \sim \frac{1}{R} \exp(ik_nR)f_n(\vartheta, \varphi). \quad (6)$$

The cross section for excitation in a state  $n$  is

$$\sigma_n = \frac{k_n}{k_0} \int_{\Omega} |f_n(\vartheta, \varphi)|^2 d\Omega. \quad (7)$$

The amplitudes are obtained by examining the asymptotic behavior of the solution of the coupled equations (4).

Two expansions have proved useful in the solution of these equations: (a) atomic basis functions and (b) molecular basis functions. Case (a) is appropriate in fast collisions where  $\tau \gg 1$  or when the influence of one atom on the other is only a small perturbation, which means that  $V$  must be small. If the incoming wave is assumed to be a plane wave and if exchange is neglected, one gets the very familiar form of the plane wave Born approximation (PWBA) with the

scattering amplitude

$$f_n(\mathbf{k}_0 - \mathbf{k}_n) = -\frac{M}{2\pi} \int \langle \psi_n | V | \psi_0 \rangle \exp[i(\mathbf{k}_0 - \mathbf{k}_n) \cdot \mathbf{R}] d\mathbf{R}. \quad (8)$$

For the matrix elements  $\langle \psi_n | V | \psi_0 \rangle$  atomic wave functions with different sophistication like hydrogenic screened, Dirac-Fock-Slater, Dirac-Fock, etc., are used. Equation (8) and related approximate formulas are applied to calculate various excitation cross sections [1].

Case (b) is appropriate when the electronic wave functions change during the collision. In Eq. (4) the first term on the right-hand side is zero if molecular wave functions are used as a basis. This coupled set of differential equations analogous to Eq. (4) is the perturbed stationary state method (pss) of Mott and Massey [2]. This method has been used to describe excitation and charge transfer in very slow atom-atom collisions.

In addition to PWBA and tractable forms of pss several influences have been discussed, although some of them already mix with the picture of the classical motion of the nucleus. (i) Increased binding of the electrons in the collision; (ii) Polarization of the electron clouds (both corrections for PWBA only); (iii) Coulomb deflection of the ion, and (iv) Relativistic influences.

Figure 1 gives an example of the influences of these effects in the total  $K$  x-ray production cross sections for  $F \rightarrow Z_2$  ( $Z_2 = 20-60$ ) at 20 MeV impact energy

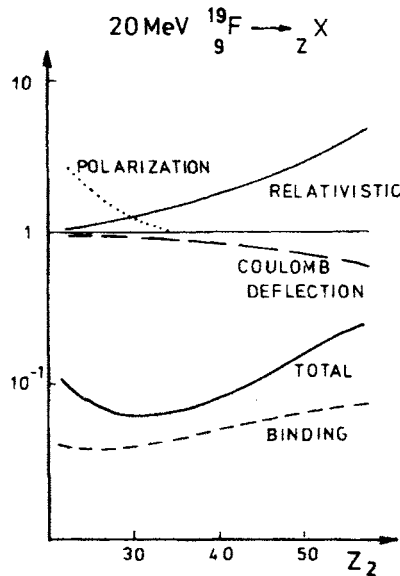


Figure 1. Correction factors for polarization, Coulomb deflection, binding, and relativistic effects in  $F \rightarrow Z_2$   $K$ -shell ionization total cross section. All correction factors are given with regard to PWBA cross sections (from Ref. 3).

which is taken from the paper of Knaf et al. [3]. All correction factors are given with regard to PWBA cross sections. Because we are here especially interested in relativistic effects, one sees that this contribution strongly increases for higher  $Z$ ; at  $Z_2 = 60$ , one already has a factor of 6. If one uses instead of  $F(Z = 9)$  a charge which is much higher, this factor can go up to  $10^4$  or  $10^5$ . This is the reason why the  $K$  ionization cross section even in very high  $Z$  collision systems (at least for small impact parameters) still is in the order of a few percent, although the binding becomes very strong.

### 3. Classical Treatment of Nuclear Motion

If the nuclear motion is treated classically, the Schrödinger (Dirac) equation for the electrons is time dependent

$$\left( H_e(t) - i \frac{\partial}{\partial t} \right) \psi(\mathbf{x}, t) = 0. \quad (9)$$

The Hamiltonian  $H_e$  for the  $N$  electrons with coordinates  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$  is

$$H_e(t) = \sum_{i=1}^N \left( -\frac{1}{2} \nabla_i^2 - \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A(t)|} - \frac{Z_B}{|\mathbf{r}_i - \mathbf{R}_B(t)|} \right) + \sum_{i < j}^N r_{ij}^{-1}. \quad (10)$$

The theory must be Galileo invariant; i.e., the classical trajectory formulation must be independent of an internal reference frame. The so-called translational factor

$$u = \exp \left[ -i \left( \sum_{k=1}^N \mathbf{v} \cdot \mathbf{r}_k - \frac{N}{2} v^2 t \right) \right], \quad (11)$$

accounts for the electronic energy and linear momentum associated with the translational motion of two reference frames with relative velocity  $\mathbf{v}$ . The translational factor must be multiplied to the separated atom solutions  $\varphi_n^A(\mathbf{x}_A)$  and  $\varphi_n^B(\mathbf{x}_B)$  to meet the boundary conditions. Thus the asymptotic form of the wave function  $\psi$  is thus given in terms of traveling separated atom states

$$\begin{aligned} \psi(\mathbf{x}, t) |_{t \rightarrow -\infty} = & \varphi_n^A(\mathbf{x}_A) \exp \left( -i \sum_{k=1}^{N_A} \mathbf{v}_A \mathbf{r}_k \right) \exp \left[ -i (E_n^A - \frac{1}{2} N_A v_A^2) t \right] \\ & + \varphi_n^B(\mathbf{x}_B) \exp \left( -i \sum_{k=N_A+1}^N \mathbf{v}_B \mathbf{r}_k \right) \exp \left[ -i (E_n^B - \frac{1}{2} N_B v_B^2) t \right]. \end{aligned} \quad (12)$$

The time-dependent electronic wave functions depend on the nuclear position and velocity vectors.

A solution of the time-dependent Schrödinger (Dirac) equation (9) can be achieved in three ways: (a) direct numerical integration; (b) using a variational procedure, and (c) expansion in known basis functions.

Method (a) has just become interesting because it needs large and fast computers. For details and first results for non relativistic  $H^+ - H$  collisions at

<30 keV with impact parameter  $b = 0$  see Ref. 4. Very recently, the first results for one-electron systems with  $b \neq 0$  were published by Bottcher [5].

Method (b) has been used up to now only by Kleber and Zwiegel [6] in the nonrelativistic form and Krause and Kleber [7] in the relativistic form for  $K$ -shell ionization. Their main problem is to find a relevant parametrization to describe the time dependence of the wave functions. Once this is chosen, a variational calculation determines the parameters as a function of time and thus the wave functions. It has been shown [6] that the wave functions more or less follow the time-independent correlation diagram energy eigenvalues in the first half of the collision but strongly deviate for higher-impact energies in the second half of the collision.

Method (c) is the well-known procedure usually used in quantum-chemical calculations. The wave functions are expanded in basis functions  $\chi_k(\mathbf{x}, t)$

$$\psi(\mathbf{x}, t) = \sum_k c_k(t) \chi_k(\mathbf{x}, t). \quad (13)$$

If this *Ansatz* is inserted in Eq. (9), we get the well-known coupled set of differential equations, which in matrix formulation are usually written

$$i\mathbf{S} \frac{d}{dt} \mathbf{C} = \mathbf{M} \mathbf{C}, \quad (14)$$

where  $\mathbf{C}$  the column matrix of the coefficients  $c_k$ ,  $\mathbf{S}$  is the overlap matrix with elements  $S_{kl} = \langle \chi_k | \chi_l \rangle$ , and  $\mathbf{M}$  is the coupling matrix with elements

$$M_{kl} = \langle \psi_k | H_e - i(\partial/\partial t)_{\mathbf{x}} | \chi_l \rangle.$$

Again as in Sec. 2 one has two possibilities: (a) expansion in atomic eigenfunctions, which is good for  $Z_A \ll Z_B$  and  $v_I \gg v_{ei}$  and (b) expansion in molecular eigenfunctions, which is good for  $Z_A \approx Z_B$  and  $v_I < v_{ei}$ .

If method (a) is used, such approximations as, for example, the impact parameter Born approximation and the semiclassical approximation (SCA) can be derived [1].

If method (b) is used, the molecular eigenfunctions  $\varphi_n$  are obtained from the solution of

$$H_e \varphi_n(\mathbf{r}, \mathbf{R}) = E_n(R) \varphi_n(\mathbf{r}, \mathbf{R}). \quad (15)$$

The energy eigenvalues  $E_n(R)$  are usually shown in the so-called correlation diagrams. Figure 2 shows a very simple very schematic nonrelativistic diagram and Figure 3 shows a complicated relativistic correlation diagram. The wave function of the time-dependent problem is then given by

$$\begin{aligned} \psi(\mathbf{r}, t) = & \sum_n c_n(t) \varphi_n(\mathbf{r}, \mathbf{R}) \exp [ig(\mathbf{r}, \mathbf{R}) \mathbf{v} \cdot \mathbf{r}] \\ & \times \exp \left( -i \int_{-\infty}^t \varepsilon_n dt' \right), \end{aligned} \quad (16)$$

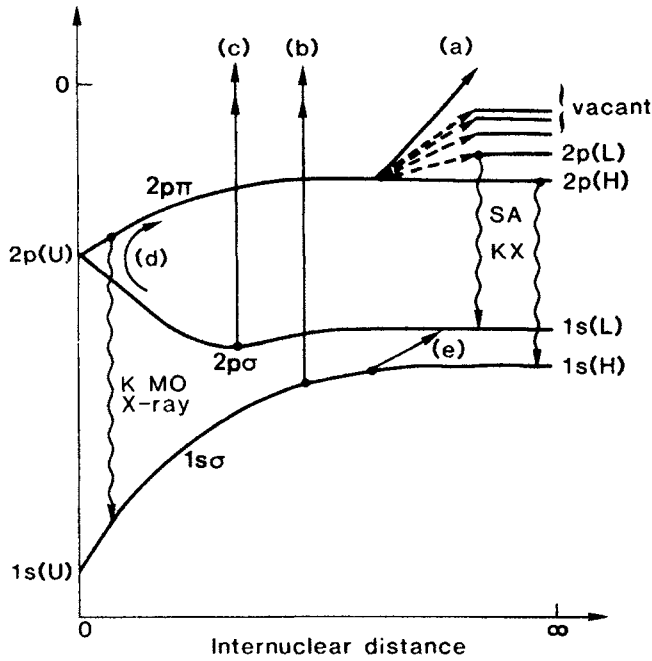


Figure 2. Schematic correlation diagram. Processes (a)–(c) indicate direct ionization, (d) rotational coupling, and (e) radial coupling (vacancy sharing).

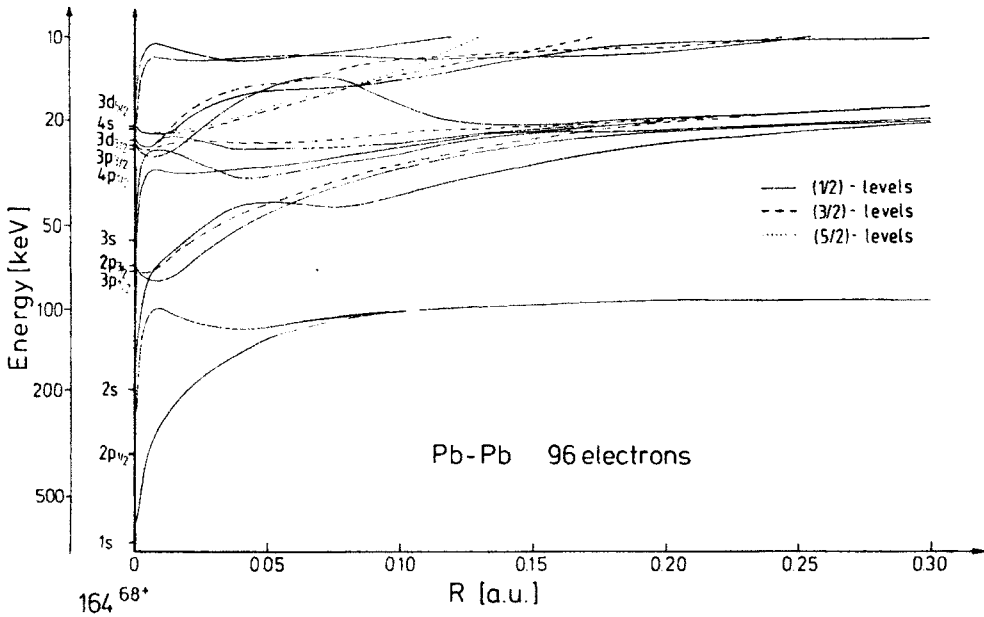


Figure 3. Relativistic many-electron self-consistent-charge correlation diagram for Pb—Pb with 96 electrons. Levels: (—) 1/2; (---) 3/2; (···) 5/2.

and the coupled set of differential Eqs. (14) has to be solved to determine the  $c_n(t)$ .  $g_n$  is a function in the translational factor, which at  $t \rightarrow -\infty$  is one but which can go to zero for small internuclear distances. In very slow collisions one may expand the translational factor in powers of  $v$ . Retaining only the lowest-order term one gets  $S_{kl} = S_{kl}$  and

$$M_{kl} = -i \left\langle \varphi_k \left| \frac{\partial}{\partial t} \right| \varphi_l \right\rangle \exp \left( i \int^t (E_k - E_l) dt' \right).$$

The matrix element  $\langle \varphi_k | (\partial/\partial t) | \varphi_l \rangle$  can be rewritten

$$\dot{R} \left\langle \varphi_k \left| \frac{\partial}{\partial R} \right| \varphi_l \right\rangle + \frac{bv}{R^2} \langle \varphi_k | L_x | \varphi_l \rangle, \quad (17)$$

where the first part usually is called the radial and the second part the rotational coupling matrix element. ( $L_x$  is the angular momentum operator perpendicular to the collision plane.)

#### 4. Discussion

The most famous example for this radial and rotational coupling is the two-state  $2p_\pi - 2p_\sigma$  rotational coupling for small  $Z$  systems [8] where an initial hole from the heavier ( $H$ ) atomic  $2p$  shell is transferred at the united ( $U$ )  $2p$  level to the lighter ( $L$ )  $1s$  level in the outgoing channel. This is process  $d$  in Figure 2 which is a very simple schematic correlation diagram. Processes  $a$ ,  $b$ , and  $c$  are direct ionization processes that are described in Sec. 2. (The electrons which are emitted here usually are called  $\delta$  electrons.) Process  $e$  is the so-called vacancy sharing which is just the radial coupling between the two outgoing  $1s$  levels.

Experiment and theory agree relatively well for the  $2p_\pi - 2p_\sigma$  rotational coupling for small  $Z$  systems, but are not consistent for heavier systems, where relativistic effects change the simple two-state picture. Spin-orbit splitting and screening effects change this part of the correlation diagram drastically [9] for higher  $Z$ . How strong the relativistic effects really are can be seen in Figure 3, which shows the correlation diagram [10] for Pb—Pb with a united  $Z$  of 164. The spin-orbit splitting is so tremendous that the  $2p_{1/2}$  level is even below the  $2s$  united level and very far away in energy (as well as the shape of the wavefunction) from the  $2p_{3/2}$  level. Also the  $3p_{1/2}$  level is below the  $2p_{3/2}$  level at very small internuclear distances. This probably has strong effects on the matrix elements which describe rotational and radial coupling. But coupled channel calculations with good *ab initio* matrix elements and energies are not yet available.

Figure 3 is calculated using a full self-consistent charge relativistic program where 96 electrons were included. As basis functions to construct the molecular wave functions  $\varphi_n$  numerical relativistic Dirac-Fock-Slater atomic wavefunctions [11] were used. The time dependence is then treated as a coupled channel calculation.

The superheavy quasimolecular systems have been studied experimentally for several years [12]. MO x-rays as well as Auger processes in the quasimolecule, measurements of the anisotropy, and impact parameter measurements now exist in the region of large  $Z$  above 100. Within the experimental accuracy the theoretical treatments described above are at least partially able to yield a general agreement with the experimental results in this region of large  $Z$  where no stable element exists. Here relativistic effects as well as screening effects are both very important (and influence each other).

But even at the medium  $Z$  region accurate *ab initio* relativistic calculations are absolutely necessary. Figure 4 shows a comparison of experimental and theoretical cross sections of the elastic scattering of  $\text{Xe}^+ - \text{Xe}$  normalized to the cross section derived from a Lenz-Jensen potential [13] as a function of the scaled scattering angle. The influence of the electronic shell structure in the quasimolecule during the scattering can be clearly seen.

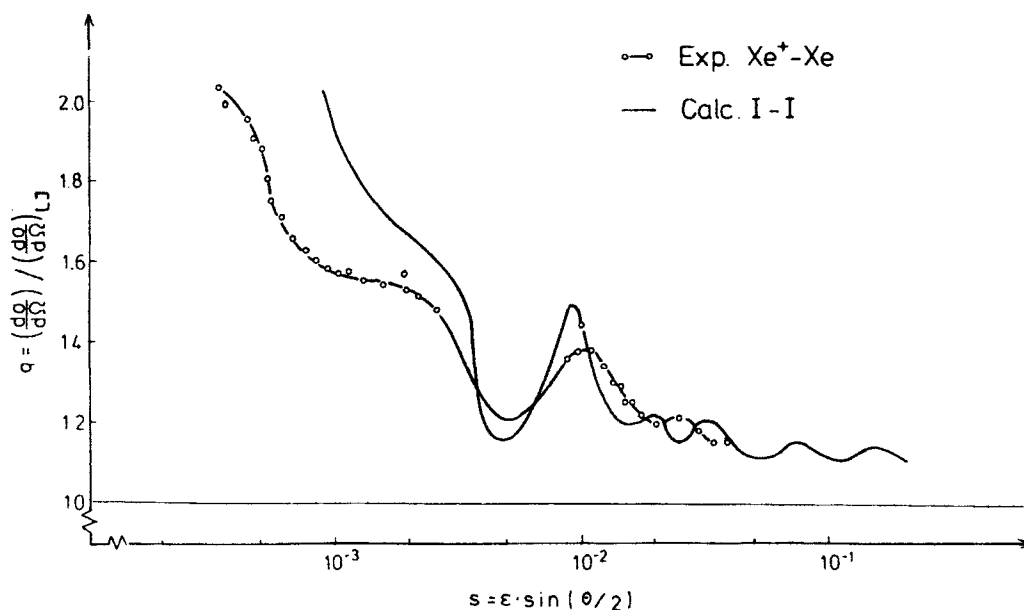


Figure 4. Differential elastic scattering cross sections for (O—O) experimental  $\text{Xe}^+ - \text{Xe}$  [13] and theory relative to the Lenz-Jensen cross section ((—) calculated I-I).

These are only a very few examples that are given to demonstrate the necessity for relativistic calculations even down to relatively small  $Z$  as well for the fact that these have to be often good, which means self-consistent, calculations.

If this is not possible or necessary, one has to be well aware of the large number of approximations that go into each of these calculations as can be seen in Secs. 2 and 3.



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