Excitation and Ionization in the Coulomb-Projected Born Approximation

SYDNEY GELTMAN

A semiclassical description is given of the Coulomb-projected Born (CPB) approximation. The applications of the CPB method to excitation and ionization of hydrogen and helium are reviewed. The improvement in describing large-angle inelastic scattering is discussed semiclassically. Reliability estimates of theoretical results are obtained by comparing Born and CPB predictions.

In this progress report we will describe the physical basis of the Coulomb-projected Born method (CPB), discuss the similarities and differences of its predictions with those of the usual Born approximation, and compare with available experimental data.

For illustration let us consider the semiclassical treatment of an electron-hydrogen atom collision. By "semiclassical" we mean that the motion of the incident electron is treated classically and the target atom is treated quantally. We may write the Hamiltonian in a manner which indicates this separation,

\[ H = T_1 - \frac{\hbar^2}{2m} v_2^2 - \frac{Ze^2}{r_2} - \frac{Ze^2}{r_1} + \frac{e^2}{r_{12}} \]  

(1)

where \( T_i \) or \( V_i \) represents a classically treated term and the explicit quantum operators denote the part treated quantally. Thus in (1) only the free-particle

SYDNEY GELTMAN • Joint Institute for Laboratory Astrophysics, National Bureau of Standards and University of Colorado, Boulder, Colorado 80302, U.S.A.
motion of the incident electron is treated classically by straight-line trajectories specifying \( r_1(t) \), and the resulting time-dependent Schrödinger equation must be solved to give the description of the excitation of the target as a result of a single impact of specified velocity and impact parameter. The most common method of solving the quantum-mechanical part of the problem is to expand in target eigenstates

\[
\Phi_p(r_2, t) = \sum_q a_{pq}(t)\psi_q(r_2) e^{-(i/E_0)t}
\]

and obtain the transition amplitudes \( a_{pq} \) by perturbation theory or the explicit solution of a coupled set of equations resulting from the truncation of the above expansion.

It is clear that our choice of how to split the total Hamiltonian in (1) is quite arbitrary. Consider the alternative of also regarding the interaction between the incident electron and nucleus as part of the classical problem,

\[
H = T_1 + V_1 - \frac{\hbar^2}{2m} \nabla_1^2 - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}
\]

Here our classical trajectory is the Rutherford trajectory of the incident electron in the nuclear field, and the quantum part of the problem is solved in exactly the same way as previously. The same type of approximation used in solving the quantum problem arising from (1) or (3) will in general lead to different transition amplitudes because of the difference in perturbation arising from the different classical trajectories for \( r_1(t) \). The extra term \(-Ze^2/r_1\) in the quantal part of (1) cannot compensate for its effect in providing a classical Coulomb trajectory in (3). In fact, it can be shown that its only effect in (1) is to change the phase of \( a_{pq} \) (for \( q \neq p \)), and thus it has no effect on transition probabilities.

Proceeding from this semiclassical picture to a fully quantum formulation, one may split the total Hamiltonian in an arbitrary way between the unperturbed part \( (H_0) \) and the perturbation \( (H') \). The most common choice for this division is to take the unperturbed part to consist of a noninteracting incident electron and target atom.

\[
H_0 = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{Ze^2}{r^2}
\]

\[
H' = -\frac{Ze^2}{r_1} + \frac{e^2}{r_{12}}
\]

When this is put into the integral form of the Schrödinger equation containing the scattering boundary condition,

\[
\Psi^\prime_p(r_1, r_2) = \Psi_0(r_1, r_2) + (E - H_0 + i\epsilon)^{-1} H' \Psi^\prime_p(r_1, r_2)
\]

(5)
the excitation amplitude takes the exact integral form

$$ f_{pq}(k_q) = -\frac{1}{2\pi} \left< e^{i k_q \cdot r_1} \psi^+_p(r_2), \left(-\frac{Z e^2}{r_1} + \frac{e^2}{r_{12}}\right) \Psi^+_p(r_1, r_2) \right> $$

(6)

In complete analogy to the semiclassical development in terms of (3), we may also choose to include the $-\frac{Z e^2}{r_1}$ term in the unperturbed part of the full quantum Hamiltonian, that is, let

$$ H_0 = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Z e^2}{r_1} - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{Z e^2}{r_2} $$

$$ H' = \frac{e^2}{r_{12}} $$

(7)

The corresponding exact integral form for the excitation amplitude, obtained through use of the Coulomb Green’s function, is

$$ f_{pq}(k_q) = -\frac{1}{2\pi} \left< \psi^-_{k_q}(r_1) \psi^+_p(r_2), \frac{e^2}{r_{12}} \Psi^+_p(r_1, r_2) \right> $$

(8)

where the final-state plane wave in (6) is replaced by the Coulomb wave $\psi^-_{k_q}$. For this reason we refer to (8) as the Coulomb-projected form of the scattering amplitude. For elastic scattering ($q = p$), this form must be supplemented by the Coulomb amplitude which is contained in the unperturbed solution $\Psi_0(r_1, r_2)$ in (5).

We then obtain the usual Born approximation and the Coulomb-projected Born approximation by replacing the exact scattering solution $\Psi^+_p$ by $e^{i k_p \cdot r_1} \psi_p(r_2)$ in (6) and (8), respectively. The roles of the incident electron–nucleus interaction term ($Z e^2/r_1$) in the semiclassical and Born quantum formulations are very similar. In the free-particle formulations [(1) and (6)] that term makes a vanishing contribution to the direct excitation amplitude (because of the orthogonality of atomic wave functions). In the Coulomb trajectory (3) or Coulomb-projected Born (8) formulations, the $Z e^2/r_1$ term plays an important, nontrivial role. It thus appears that more of the essential physics of the problem is retained in the Coulomb formulations than in the free-particle formulations.

Applications of the CPB method have been made to the electron-impact excitation and ionization of hydrogen and helium in a series of papers by Geltman and Hidalgo (II, 1971; III, 1972; IV, 1974a; V, 1974b; paper I in this series concerned charge transfer, which is outside the area of this report). Paper II covers the direct excitation of the 2s, 2p, and 3s states of H, Paper III is concerned with the direct excitation of the $2^1 S$ and $2^1 P$ states of He, and papers IV and V are concerned with the triple differential ionization of H and He, respectively, including exchange effects. We are now
extending the excitation calculations to lower energies with the inclusion of exchange. The exchange amplitudes $g_{pq}$ are defined as having the form of the direct amplitudes in (6) and (8), except that $r_1$ and $r_2$ are permuted in $\Psi_p^\dagger$. Thus the Born exchange result is the Oppenheimer approximation, for which analytical expressions have been derived (Corinaldesi and Trainor, 1952; Bell, 1965), and we evaluate the CPB exchange amplitudes by numerical methods.

The most striking departures from the usual Born results are in the differential cross sections, particularly at large scattering angles. This is illustrated in Figure 1 for the $1s$–$2s$ excitation of H. The CPB result is seen to follow the Rutherford form, $\csc^4 (\theta/2)$, over a very wide range of the larger angles, while the Born result falls much more rapidly with angle.

![Figure 1. Differential cross section (in units of $a_0^2$sr) for the $1s$–$2s$ excitation of hydrogen by 200 eV electrons in the various approximations: B(E), Born (exchange); CPB(E), Coulomb-projected Born (exchange). The points are proportional to the Rutherford angular dependence, $\csc^4 (\theta/2)$, and have been normalized to the large-angle CPB results.](image-url)
Thus it is seen that the quantum-mechanical CPB result is fully consistent with the semiclassical arguments given above. Exchange effects are small at all angles for the CPB result, while they have a major effect at backward scattering angles in the usual Born approximation.

Considerable experimental data are available for the large-angle differential excitation of helium, and in Figure 2 we show a comparison with data of Opal and Beaty (1972). We have not yet evaluated the exchange contributions in helium, but there is no reason to expect those to be appreciably larger than shown for the hydrogen case of Figure 1. The significant improvement in the CPB curve over the Born curve is obvious. Similarly improved large-angle results were also obtained by Madison and Shelton (1973) using distorted wave methods. We use simple uncorrelated exponential wave functions for the helium ground and excited states, and this could give rise to an intrinsic, but we believe small, error in the results of our calculations.

Closely related to the angular variation at a given energy is the variation of $d\sigma/d\Omega$ as a function of energy at fixed angle. It may be recalled that for any nonvanishing scattering angle the Born approximation (without exchange) predicts $d\sigma/d\Omega$ to vary asymptotically as $E^{-6}$ for $s-s$ transitions and as $E^{-7}$ for $s-p$ transitions. We find from the numerical results of all

![Figure 2. Differential cross section for the $1^1S-2^1P$ excitation of helium by 200 eV electrons in Born (dashed line) and Coulomb-projected Born (solid line) approximations (exchange not included). Points are the absolute data of Opal and Beaty (1972).](image-url)
our CPB calculations that for any transition and nonforward scattering angle, the differential cross section asymptotically falls off as $E^{-3}$. This behavior is radically different from the Born prediction and can easily be understood semiclassically, where the differential cross section for the excitation $p \rightarrow q$ may be written as

$$\frac{d\sigma(p \rightarrow q)}{d\Omega} = \frac{d\sigma(\text{Rutherford})}{d\Omega} P(p \rightarrow q)$$

(9)

Here $P(p \rightarrow q)$ represents the probability of a transition due to the traversal of an incident electron on a Rutherford trajectory [as formulated in (3)]. A typical value for this transition probability is the one applicable to the CPB results in Figure 1, or $P(1s \rightarrow 2s) = 0.0058$, which would be essentially independent of scattering angle (or impact parameter) from $\theta \simeq 40^\circ$ to $180^\circ$.

Examination of the coupled equations for the transition amplitudes shows that in the high energy limit, independent of transition and of classical trajectory (see, for example, Geltman, 1969),

$$P(p \rightarrow q) = |a_{pq}(\infty)|^2 \frac{E^{-1}}{E \rightarrow \infty}$$

(10)

Combining this with the well-known $E^{-2}$ energy dependence of the Rutherford cross section gives us the overall $E^{-3}$ dependence, which we have found independently from the fully quantal CPB calculations. It is of interest to note here that an attempt at a similar treatment for the Born approximation would be meaningless for all angles other than forward scattering because the semiclassical trajectories are undistorted straight lines. Only after high-order eikonal procedures or the evaluation of higher-order terms in the Born series could one expect to obtain the correct large-angle behavior.

An illustration of the results for total excitation cross section is given for the $1s$–$2s$ case of hydrogen in Figure 3. The detailed numerical results show that both direct approximations (B and CPB) and both exchange approximations (BE and CPBE) become equal to within 1\% at about 100 eV, while the total exchange contribution reaches the 1\% level at about 600 eV. Thus the large differences between the CPB and Born differential cross sections at large angles (Figure 1) do not show up at all in the integrated cross section at 200 eV. Rather, the main contribution to the total cross sections comes from $\theta = 0^\circ$ to $30^\circ$, where it can be seen that the two direct and the two exchange approximations become indistinguishable. We interpret the near equality of CPB and Born amplitudes as an indication of the correctness of both, because use of the correct $\Psi^+_p$ in (6) and (8) would yield the same (exact) amplitude. On the other hand, when they are not equal, such as in the large-angle case, we regard the CPB result as the more reliable, although we lack an independent theoretical criterion to predict the degree of reliability.
The experimental curve (as a relative measurement) shown in Figure 3 has been obtained by Lichten and Schultz (1959), Stebbings et al. (1961), Hils et al. (1966), and Kauppila et al. (1970). The three latter measurements also revealed a large (apparent) cascade contribution over a large range of energies starting at about 50 eV. In Figure 3 we have normalized the measurements to the CPBE calculation at about 45 eV. We believe this value to be correct to the order of 3% because of its confluence with the BE value. If we accept this normalization, the extreme low-energy behavior of the cross section is consistent with the close-coupling results just above threshold. It is interesting to note that Lichten and Schultz originally normalized their data to the Born value (without exchange) at this low energy. Although at that time there was little reason to believe the Born approximation to be valid at 45 eV, it is our present conclusion that, except for a 5% exchange contribution, it is essentially correct for this transition. Of course, it does not follow that the Born approximation is valid to such low energies for all transitions.

Our final application of the Coulomb-projected Born method is to the triple differential ionization of H and He. This cross section, $d^3\sigma/d\Omega_a d\Omega_b dE_a$, is proportional to the probability of ionizing the atom, with the two final electrons going into specified elements of solid angle and energy. Only one of the elements of energy need be specified, since the other will be fixed by
energy conservation. Ehrhardt et al. (1972a,b) have made extensive measurements of this quantity for the case in which the incident and the two final electrons are all in the same plane. A sampling of their results and our calculations is given in Figure 4. It can be easily proved that the Born result must be symmetric about the electron momentum transfer vector, completely independent of the sophistication of the atomic wave functions used. In most cases the data show a forward peak which is displaced to larger angles, and also a ratio of forward-to-backward peak magnitude which is in disagreement with the Born values. We note a substantial improvement in representing both of these properties in the CPBE approximation. The effect of exchange in most of the cases is generally small, so that the differences in the theoretical curves in Figure 4 are due to the differences in the basic scattering approximation. The Born approximation is best for the case of high incident energy and small scattering angle (\(E_a = 256.5\) eV, \(\theta_a = 4^\circ\)), as might be expected. Again, the simplest type atomic wave functions were used here to represent the bound and ionized states of helium.

In summary, we are encouraged by the consistently improved agreement with experiment that is attainable with the use of the Coulomb-projected Born approximation. This improvement appears to persist down to energies as low as 40 eV in some cases. We are continuing to investigate the role of exchange and the coherent excitation properties in this approximation.

References


Figure 4. Triple differential cross sections (in units of \(a_0^3/\text{sr}^2/2\) ry) for the coplanar ionization of helium at various incident energies \((E_a)\), fixed angles \((\theta_a)\) for one of the emerging electrons, and energies \((E_b)\) of the other emerging electron. Solid line, Born; dashed line, Coulomb-projected Born exchange. The experimental points are the relative data of Ehrhardt et al. (1972a,b) normalized to the CPBE calculation in the vicinity of the forward peak.