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Classical-Quantum Correspondence for Ionization in Fast Ion-Atom Collisions

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Abstract. We analyze the interplay between classical and quantum dynamics in ionization of atoms by fast charged particles. The convergence to the classical limit is studied as a function of the momentum transferred to the electron during the collision, the impact parameter, the energy and angle of the emitted electron, and the initial state of the target. One goal is to assess the validity of exact classical (CTMC) methods and approximate classical models such as the Thomson model. Applications to data for electron ejection at large angles are presented. The connection between collisional ionization by charged particles and ionization by half-cycle pulses is discussed.

1. Introduction

The theoretical understanding of ionization caused by strong and non-periodic pulses is of fundamental interest. Such pulses can be delivered either by the time-dependent Coulomb field of fast ions passing by an atom or by ultrashort laser pulses with durations corresponding to a fraction of an optical cycle. For fast ion-atom collisions, well established approximations exist at high impact velocities (v_p) or small projectile charges (Z_p) for which the interaction of the target with the impinging ion can be treated as a small perturbation. For collision velocities comparable to the orbital velocity of target electrons and projectile charges of the order of or greater than the target nuclear charge (Z_t), more elaborate approaches are necessary which can treat the target and projectile nuclear fields on equal footing and can account for the strong coupling among all reaction channels. It is under these circumstances that classical trajectory Monte Carlo (CTMC) methods[1-3] have become widely and successfully utilized. The principal assumption underlying these models is that during and after the collision all interacting particles evolve classically in time. Quantum mechanical features enter solely via the initial boundary conditions of the evolution, i.e. the atomic initial state.

A detailed understanding of the range of validity of these methods is of considerable interest for both fundamental and application oriented reasons. For example, with the availability of state-selectively excited Rydberg states

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with sufficiently high target densities, the study of ion-Rydberg atom collisions has become routine [4,5]. In this regime, full quantum calculations are difficult to perform while the validity of classical methods for state-selective processes has not yet been established. Similarly, most non-perturbative calculations for energy loss of multiply charged particles in condensed matter employ classical approximations. For channeled particles, successive collisions with lattice atoms probe the “local”, i.e. impact parameter dependent, energy transfer and ionization probability. The validity of classical methods for impact parameter specific processes remains an open question. Most recently, with advances in short-pulse laser technology the perturbation of atoms exposed to strong and ultrastrong laser fields has gained considerable attention[6]. As classical methods are, unlike quantum treatments, readily applied to atoms in strong electromagnetic fields, delineation of their validity as well as of their limitations are of considerable interest.

We focus in the following on the atomic response to a short but strong impulsive perturbation which is caused by the passing-by of a charged particle in fast ion-atom collisions or by an ultrashort half-cycle electromagnetic pulse. This regime is to be distinguished from low- to intermediate velocity atomic collisions or long laser pulses containing many optical cycles. We present an analysis of the classical character and limit of the quantum mechanics of ionization. We analyze the existence of a classical limit as a function of different parameters and identify regions in parameter space in which classical results mimic their quantum counterparts. We apply our analysis to two problems: the ejection of electrons into large angles in ion-atom collisions and the thresholds for ionization by ultrashort half-cycle electromagnetic pulses. Atomic units will be used throughout.

2. Classical Limit of the Liouville-Von Neumann Equation

Different equivalent formulations of classical dynamics can be recovered as the respective classical limit, formally to be taken as $\hbar \rightarrow 0$, of corresponding equivalent formulations of quantum dynamics. Such correspondences exist, for example, between Heisenberg’s equation of motion and Hamilton’s equation of motion or the Schrödinger equation and the Hamilton-Jacobi equation.

In principle, any of these approaches can be used to quantitatively explore the existence of and convergence to the classical limit. In practice, however, a judicious choice of the starting point on the quantum level is required since this limit is highly singular and non-uniform. One frequently explored avenue is the Feynman path integral approach[7] (Feynman propagator) whose semiclassical limit was given by Van Vleck[8] (Van Vleck propagator). It allows the decomposition of the S matrix and of the transition amplitude in terms of a classical transition amplitude multiplied by a the phase factor containing the classical action [9],

$$S_{i \rightarrow f} = \sum_{\alpha} (p_{ci}^{\alpha}(i \rightarrow f))^{1/2} \exp \left[\frac{i}{\hbar} F_4(i, f, \alpha) \right], \quad (1)$$

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where F_4 is the reduced action along the classical path with path index α connecting the initial (i) and final (f) states and $p_{cl}^\alpha(i \rightarrow f)$ is the classical probability for the transition. Eq.(1) contains the so-called "primitive" semiclassical path interferences when more than one classically allowed path α connects the initial with the final state. For illustrative purposes we have displayed in Eq.(1) the $\hbar$ dependence of the interference phase to highlight the essential singularity of the classical limit as $\hbar \rightarrow 0$. Classical dynamics is therefore only recovered upon averaging $|S_{i \rightarrow f}|^2$ over infinitely rapidly oscillating phases by averaging (summing) over the initial (final) state variables which become continuous in the classical limit. The approach of the classical limit involves therefore non-commuting limiting operations of $\hbar \rightarrow 0$ and the long-time limit $t \rightarrow \pm\infty$, where from the latter quantization conditions of initial and final states are to be recovered. Despite the complexity of this task, considerable progress has been made along those lines [9].

We choose in the following a different approach which is based on the quantum dynamics of the density (or statistical) operator and its correspondence to classical phase space dynamics [10,11,12]. The density operator satisfies the Liouville-Von Neumann equation

$$i \frac{d}{dt} \hat{\rho} = [\hat{H}, \hat{\rho}]. \quad (2)$$

We denote in the following quantum variables by hats to distinguish them from the corresponding classical variables. The connection to the classical phase space flow is made through the Wigner function f_W , the Weyl transform of the coordinate representation of the density matrix, $\langle \vec{r} - \vec{s}/2 | \hat{\rho}(t) | \vec{r} + \vec{s}/2 \rangle$,

$$f_W(\vec{r}, \vec{p}, t) = \frac{1}{(2\pi)^3} \int d^3 s \, e^{-i\vec{p}\vec{s}} \langle \vec{r} - \vec{s}/2 | \hat{\rho}(t) | \vec{r} + \vec{s}/2 \rangle. \quad (3)$$

Application of the Liouville-Von Neumann equation to (3) leads to the quantum Liouville equation for the Wigner function.

$$\frac{\partial f_W}{\partial t} = \hat{L} f_W = -\vec{p} \cdot \nabla_{\vec{r}} f_W + \frac{2}{\hbar} \sin \left(\frac{\hbar}{2} \nabla_{\vec{r}} \cdot \nabla_{\vec{p}} \right) f_W U \quad (4)$$

where the operator $\nabla_{\vec{r}}$ in the argument of the sine function is understood to act only on U while $\nabla_{\vec{p}}$ acts on f_W . Since we are interested in the $\hbar \rightarrow 0$ limit, we have explicitly displayed the dependence of Eq.(4) on $\hbar$.

The Wigner function is related to the diagonal elements of the density matrix, i.e. the densities in coordinate and momentum space by [10]

$$\hat{\rho}(\vec{r}, t) = \int d^3 p \, f_W(\vec{r}, \vec{p}, t) \quad (5)$$

$$\hat{\rho}(\vec{p}, t) = \int d^3 r \, f_W(\vec{r}, \vec{p}, t). \quad (6)$$

Furthermore, in the case the density operator represents a pure state, the action can be recovered in the semiclassical limit from the momentum vector field

$$\langle \vec{p} \rangle_{\vec{r},t} = \nabla_{\vec{r}} S(\vec{r},t) = \frac{1}{\rho(\vec{r},t)} \int d^3 p \vec{p} f_W(\vec{r}, \vec{p}, t), \quad (7)$$

where $S(\vec{r},t)$ is the phase of the wavefunction defined by $\psi(\vec{r},t) = |\psi(\vec{r},t)| e^{iS(\vec{r},t)}$. The phase $S(\vec{r},t)$ corresponds to the classical action provided the momentum vector field is single-valued. Since, typically, momentum vector fields are either multi-valued functions of $\vec{r}$ or do not even form a smooth Lagrangian manifold in non-separable systems, a more useful interpretation of Eq.(7) is that of a local expectation value of the momentum operator at $\vec{r}$.

The classical limit follows now formally from expanding the sine operator in Eq. 4 and keeping only the first term. The result is the classical Liouville equation

$$\frac{\partial f}{\partial t} = L f = -\vec{p} \cdot \nabla_{\vec{r}} f + \nabla_{\vec{r}} U \cdot \nabla_{\vec{p}} f \quad (8)$$

where L is the classical Liouville operator and $f(\vec{r}, \vec{p}, t)$ is the corresponding phase space distribution function of the electron. Note that in natural units this expansion can be recognized as an expansion in ascending powers of $\hbar$. Accordingly, Eq. (8) neglects terms of the order of $O(\hbar^2)$. Eq.(4) possesses, unlike Eq.(1), a convergent classical limit $\hbar \rightarrow 0$ and provides therefore a convenient starting point for the quantitative analysis of the classical-quantum correspondence. However, the complications with the singular behavior and the non-commutativity of the limits $\hbar \rightarrow 0$, $t \rightarrow \infty$ are preserved and reappear in the asymptotic initial conditions or final state representations of Eq.(4). The proper initial conditions for $t \rightarrow -\infty$ are stationary quantum density matrices which contain $\hbar$ to all orders through, in the semiclassical limit, quantization conditions of the form

$$\frac{1}{\hbar} \oint \vec{p} d\vec{r} = 2\pi(n + \beta) \quad (9)$$

(β : Maslov index). One consequence of this difficulty is, that the Wigner function (Eq.(3)) does not, in general, provide appropriate initial conditions for the classical Liouville equation. For example, the Wigner distribution for an isolated hydrogen atom becomes dynamically unstable when its evolution is calculated using the classical Liouville equation in absence of any perturbation. Thus, additional approximations are necessary to describe the initial phase-space distribution of the electron. The simplest and most frequently used initial phase-space distribution which is dynamically stable is the microcanonical ensemble proposed by Abrines and Percival [1].

$$f_i(\vec{r}, \vec{p}) = k \delta[E_i - p^2/2 + 1/r] \quad (10)$$

where $k = (-2E_i)^{5/2}/(2\pi)^3$ is a normalization constant. One of the most important properties of this distribution is that it exactly reproduces the momentum distribution of a statistical average of states of a given shell with principal quantum number n_i and binding energy $E_i = -1/(2n_i^2)$. Its

position distribution, however, does not mimic the quantal probability distribution. The disagreement is most obvious in the classically forbidden region where Eq.(10) vanishes identically. A better representation of both the position and the momentum distributions can be achieved using a superposition of microcanonical ensembles with binding energies around E_i [13,14,15] however at the expense of an incorrect initial state energy distribution. The CTMC method [1-3] is simply a Monte Carlo technique to solve the classical Liouville equation (Eq.(8)) with compatible initial conditions such as Eq.(10). We refer to the CTMC method as an exact classical method since it solves the Liouville equation without involving further approximations to the dynamical evolution.

For short impulsive perturbations by fast collisions another property of the quantum and classical Liouville equations (Eq.(5,9)) is of crucial importance: For short interaction times or large collision velocities ($v_p^{-1} \rightarrow 0$) classical and quantum mechanical variations of the position probability density and mean velocity field (i.e. Eqs. 5 and 7) agree with each other up to second order in v_p^{-1} . The solution of the quantum Liouville equation after a short-time interaction (from $-T$ to T) with a fast moving projectile is given by [11],

$$f_q^{(1)}(r, p, T) = f_q(r, p, -T) + \frac{1}{v_p} \int_{-v_p T}^{+v_p T} dz'_p W_q(z'_p) f_q(r, p, -T) \quad (11)$$

with

$$W_q(z_p) f_q = 2 \sin \left(\frac{1}{2} \nabla_r \cdot \nabla_p \right) f_q U_q(|r - b - z_p \hat{z}|). \quad (12)$$

where $z_p = v_p t$, $\vec{b}$ the impact parameter and $f_q^{(1)}$ denotes a first-order solution in powers of v_p^{-1} and we have used $(L_q - W_q) f_q(r, p, -T) = 0$. Consequently, the mean momentum transfer is given by

$$\Delta \vec{p}^{(1)}(r) \simeq \frac{1}{v_p} \lim_{v_p \rightarrow \infty} \int_{-v_p T}^{v_p T} dz_p \nabla_r U_p(|r - b - z_p \hat{z}|) \quad (13)$$

which agrees exactly with the corresponding classical result. This correspondence is completely analogous to the equivalence of the full Feynman propagator and the semiclassical Van Vleck propagator for infinitesimally small time intervals. As we anticipate from Eq.(13) and will illustrate in more detail below, the collisional momentum transfer $\Delta \vec{p}^{(1)}$ plays the role of a characteristic parameter in quantitatively elucidating the classical-quantum correspondence.

The following simple criteria can be formulated for which the convergence to the classical limit is expected. For the asymptotic initial and final states with (rationalized) De Broglie wavelength $\lambda_{i,f}$ and radii $\langle r \rangle_{i,f}$ we expect

$$\lambda_{i,f} \ll \langle r \rangle_{i,f} \quad (14a)$$

which reduces for hydrogenic states to the requirement of large quantum numbers

$$n_{i,f} \gg 1. \quad (14b)$$

The dynamical evolution during the collision is expected to proceed classically "on the average" if

$$\lambda_{\Delta p} \ll \langle r \rangle_{i,f} \quad (15a)$$

where $\lambda_{\Delta p} = 1/\Delta p$ is the wavelength of the impulsive perturbation probing the internal structure of the atom. For hydrogenic systems Eq.(15a) becomes

$$\Delta p n^2 \gg 1. \quad (15b)$$

If classical dynamics is sensitive to the internal structure of atoms on a length scale r_c small compared to the mean radius, $\langle r \rangle$ must be replaced by r_c in Eq.(15a). Furthermore, in elucidating the classical-quantum correspondence, the classical scaling invariance is very useful. Scaling invariances are based on the fact that the classical equations of motion are invariant under the scaling transformation $\vec{r}' = \vec{r}/n^2$, $\vec{p}' = \vec{p}n$, $t' = t/n^3$ [1,16] where n is in general an arbitrary scaling parameter. Our choice of the symbol indicates that we will use the principal classical action (principal quantum number) as the scaling parameter, i.e. we investigate the n dependence of the scaled dynamical observable. Upon proper scaling, classical dynamics is independent of n . Quantum corrections break the scaling invariance. Any remaining n dependence of quantum observables not accounted for by classical scaling is therefore a clear signature of non-classical contributions (i.e., the discreteness of n). In this context we introduce the scaled momentum transfer

$$\Delta p_0 = \Delta p / \langle p \rangle_i = n_i \Delta p \quad (16)$$

in units of the average orbital momentum of the initial state.

3. Slingshot Effect and Classical Impulse Approximation

Many features of the classical-quantum correspondence can be intuitively understood in terms of the slingshot effect wellknown from planetary science. One of the fastest and most efficient ways to transport a space probe (in atomic physics, the electron) to the outer fringes of the solar system and beyond (i.e., ionization) is to choose such an initial elliptic orbit around the sun (the nucleus) after take-off that features a (relatively) close encounter with another planet (the projectile) (Fig. 1). Within this three-body system of sun, planet and space probe, a two-body elastic collision between the space probe and the planet can lead to an energy gain of the two-body system (space probe-sun) such that the space probe acquires enough energy to leave the solar system (ionization). This turns out to be the essence of the description of ionization in fast collisions within classical dynamics.

FIGURE 1. The planetary slingshot effect: Kepler ellipse of a space probe (i.e. electron) around the sun (nucleus) perturbed by an impulsive momentum transfer by Jupiter (incoming charged particle).

The slingshot transfers energy and angular momentum to the electron which are given by

$$\begin{aligned}\Delta E &= \frac{1}{2}(\vec{p}(\vec{r}) + \Delta \vec{p})^2 - \frac{1}{2}\vec{p}(\vec{r})^2 \\ &= \Delta \vec{p} \vec{p}(\vec{r}) + \frac{1}{2}\Delta p^2\end{aligned}\tag{17}$$

and

$$\Delta \vec{L} = \vec{r} \times \Delta \vec{p}\tag{18}$$

where $\Delta \vec{p}$ is the momentum transferred to the electron by the passing by the projectile. Eqs.(17,18) correspond to the classical impulse approximation. Its validity hinges on the short interaction time T with the projectile on the time scale of the orbital period $T_n = 2\pi n^3$, i.e.

$$T/T_n = T_0 \ll 1\tag{19}$$

In the example of Fig. 1, the validity of Eq.(19) follows from the small mass ratio of Jupiter to sun, $M_j/M_s \approx 10^{-3}$. Only in the immediate vicinity of the Jupiter during a fraction $\sim (M_j/M_s)^{1/2}$ of the orbital period the perturbing force by Jupiter dominates over the gravitational attraction by the sun during which the momentum (Eq.(19)) is being transferred. For charged particle impact, the criterion (21) is satisfied if the collisions are fast (i.e.,

$v_p^{-1} \rightarrow 0$). The important feature of the energy gain (or loss) by the slingshot (Eq.(17)) is the presence of a term dependent on the coupling of the local momentum on the orbit, $\vec{p}(\vec{r})$, at the point of the collision to the momentum transfer $\Delta\vec{p}$. This slingshot term is at the heart of both the success and the failure of classical approximations of the collisions. Estimating $|p(\vec{r})|$ by the average momentum $\langle p \rangle_i = n_i$, this term dominates in the energy transfer for small scaled momentum transfers

$$\Delta p n_i = \Delta p_0 \ll 1. \quad (20)$$

4. The Impulsively Perturbed Hydrogen Atom

We analyze first the impulsively perturbed (“kicked”) hydrogen atom. i.e. a hydrogen atom subject to an instantaneous momentum transfer (or “kick”) $\Delta\vec{p}$ which occurs at a time t_0 . The Hamiltonian for this problem is[12]

$$H = \frac{p^2}{2} - \frac{1}{r} - \vec{r} \cdot \Delta\vec{p}\delta(t - t_0) \quad (21)$$

where $\vec{p}$ and $\vec{r}$ are the momentum and position vectors of the electron and we have assumed an infinitely massive nucleus. Eq.(21) can model realistic collision systems for fast projectiles for which the duration of the perturbing pulse is short compared to the characteristic times (inverse frequencies) of the atomic system analogously to the gravitational slingshot discussed above. The beauty of the simple model described by Eq. 21 is the availability of exact solutions in both classical and quantum mechanics. The correspondence can therefore be investigated without resorting to any approximation. If we denote by $\psi(\vec{r}, t_0^-) = \phi_i(\vec{r})$ the wavefunction of the electron just before the kick, the exact wavefunction just after the kick will be

$$\psi(\vec{r}, t_0^+) = e^{i\Delta\vec{p} \cdot \vec{r}} \psi(\vec{r}, t_0^-), \quad (22)$$

i.e. the matrix elements of the time evolution operator in the atomic state representations reduce to inelastic transition form factors.

$$\langle \phi_f | U(\infty, -\infty) | \phi_i \rangle = \langle \phi_f | \exp(i\Delta p \cdot r) | \phi_i \rangle \quad (23)$$

Analytic expressions for this integral for arbitrary initial and final states can be found elsewhere [17]. The corresponding classical problem can be solved exactly as well. For ionization of a microcanonical ensemble of a shell n_i to a final state with energy E_f , the probability per unit energy interval is given by

$$\frac{dP_n^{CI}}{dE_f} = \frac{8(-2E_i)^{5/2}(\Delta p)^5}{3\pi[(E_f - E_i + (\Delta p)^2/2)^2 - 2(\Delta p)^2 E_f]^3}. \quad (24)$$

This distribution (Eq.(24)) is compared in Fig. 2 with its quantum counterpart for a hydrogen atom initially in its ground state. Since the characteristic momentum of the electron in the ground state of a hydrogenic atom is $\langle p \rangle_i = 1$ the momenta of this figure can be considered as scaled momenta Δp_0 . For $\Delta p = \Delta p_0 = 0.2$ the classical ionization probability is uniformly by far too small over the whole spectrum of energies of the emitted electron. On the other hand, for increasing values of Δp the classical ionization describes the dominant region of the spectrum increasingly accurate while discrepancies in the wings of the distribution persist.

FIGURE 2. Quantum mechanical (full curve) and classical (broken curve) ionization probability density as a function of the energy of the ejected electrons for a hydrogen atom subject to an impulsive momentum transfer (Eq.(21)).

For $\Delta p_0 \geq 3$ the probability density of ionized electrons exhibits a noticeable peak at an energy $E_f \approx (\Delta p)^2/2 + E_i$ corresponding to the mean energy transferred to the electron. In a three-dimensional plot of the yield of electrons as a function of E_f and Δp , this peak would develop into a ridge which is the equivalent of the well known "Bethe ridge" [18-20]. This ridge signifies the energy-momentum dispersion relation of a free particle. The fact that classical dynamics is able to correctly describe the width of this "binary encounter" like peak is due to the fact that the slingshot term $\vec{p} \cdot \Delta \vec{p}$ (Eq.(17)) incorporates the information on the momentum distribution (Compton profile) of the initial state into the classical description. By the same token, however, the overestimate of the low-energy spectrum for $\Delta p_0 = 10$ is also

consequence of the very same slingshot term. This discrepancy, while quantitatively unimportant since the dominant region for ionization lies at much higher energies, can, nevertheless, give important insights into differences between classical and quantal ionization: We note first that for large Δp_0 , the criterion for small wavelength of the perturbation (Eq.(15b)) is well satisfied and classical dynamics is expected to be valid "on the average." However, in order to produce a kinetically unfavored low-energy electron by a large pulse $\Delta \vec{p}$, a large orbital momentum $\vec{p}(\vec{r})$ antiparallel to $\Delta \vec{p}$ is required in the slingshot term (Eq.(17)). Since within classical mechanics the momentum distribution and position distribution are strongly correlated (via the Hamiltonian function) only segments of highly eccentric orbits at small distances from the nucleus, $r_c \ll \langle r \rangle_n$, can furnish the required large local momentum. The required distances r_c are, for large Δp compared to the mean momentum $\langle p \rangle$, smaller than

$$r_c \lesssim (\Delta p)^{-2}. \quad (25)$$

Such a tight localization is inconsistent with the uncertainty relation involving the momentum transfer (Eq.(15a)) in which we must replace $\langle r \rangle$ by r_c ,

$$\Delta r \simeq r_c \gtrsim (\Delta p)^{-1} \quad (26)$$

The strong classical $r - p$ correlation is weakened in quantum mechanics due to delocalization of the electron over the size of the De Broglie wavelength associated with the momentum transfer. This leads to quantum suppression of ionization. The complete failure of classical dynamics for small scaled momentum transfer ($\Delta p_0 = 0.2$), on the other hand, is a consequence of the violation of the criterion (Eq.(15b)) involving the average size of the charge cloud and signifies the lack of dipole-allowed transitions in classical dynamics. In the limit of soft collisions which can be viewed as the absorption of a virtual photon by the atom, the momentum transfer is too small and the associated De Broglie wavelength too large to "resolve" the internal structure of the constituents of the hydrogen atom. Instead, the virtual photon interacts with the atom as a composite system. (Free electrons do not absorb or emit photons.) Quantum mechanically, the energy-momentum dispersion relation satisfied in the transition involves now the recoil of the nucleus rather than the momentum exchange between the external field (the "kick" or the projectile) and the electron. In other words, for $\lambda_{\Delta p} \gg \langle r \rangle$; almost all energy of the virtual photon will be delivered to the electron while the corresponding momentum originates from the recoil of the nucleus. By contrast, classical dynamics requires energy and momentum transfer to the electron to be directly linked through the slingshot expression Eq.(17). Obviously, the fact that electron emission with energies large compared to $\Delta p^2/2$ occurs at all is due to the coupling term $\vec{p}(\vec{r}) \cdot \Delta \vec{p}$ which now strongly dominates.

The resulting breakdown of classical scaling invariance is shown in Fig. 3 for the ionization probability integrated over all final energies for different initial energy levels $n = 1, 3$ and 10 as a function of the scaled momentum transfer $\Delta p_0 = n \Delta p$. Note that if classical scaling invariances were to hold, results for all n -levels would lie on the same universal curve as classical results do. The larger n the larger the range of momentum transfers for which the quantum mechanical curve agrees with the scaling invariant

classical result. Fig. 3 may be viewed as an illustration of the correspondence principle at work. In the limit $n \rightarrow \infty$ the quantum results converge to the same universal curve which, moreover, coincides with the classical result. The convergence is, however, non-uniform in Δp which is the cause of the breakdown of the classical approximation for finite n levels. Eq. (15b) gives the estimate $\Delta p_0 > n^{-1}$ for the region of convergence. In addition to this necessary criterion a more stringent criterion can be derived from the slingshot relation (Eq.(17)) requiring the classical free particle energy and momentum transfer to be sufficient to overcome the energy gap of adjacent quantum levels, $\Delta E = n^{-3}$ (as $n \rightarrow \infty$). This criterion which defines the region where the discreteness of the quantal excitation spectrum becomes unimportant leads to

$$\Delta p_0 \gtrsim (1/n)^{1/2} \quad (27)$$

in agreement with the results of Fig. 3.

FIGURE 3. Quantum mechanical (full curves) and classical (broken curve) total ionization probability of a hydrogen atom in different excited levels with principal quantum number n as a function of the scaled momentum transfer $\Delta p_0 = n\Delta p$ (Eq.(21)). The classical results reduce to a single curve for all n levels.

5. Impact Parameter Dependence of Ionization

Fig. 4 displays the ionization probability for 5 MeVp + H(1s) collisions as a function of the impact parameter integrated over all energies and angles of the ejected electron. The quantum results in the first Born (B1) approxi-

FIGURE 4. Total ionization probability as a function of the impact parameter in 4 MeV $p + H(1s)$ collisions. The quantum mechanical B1 results (full curve) is compared with the CTMC results using an initial microcanonical distribution (dotted curve) and the initial distribution of Cohen [15] which reproduces the correct radial probability density of the atom (broken curve).

mation (see e.g. [21]), which is expected to be valid at this energy, is in sharp disagreement with the CTMC result over the whole range of impact parameters. The well-known failure at large impact parameters is the obvious consequence of the lack of dipole-allowed transitions in soft collisions. More interesting and less well-known is the equally drastic failure at small impact parameters. To verify whether this disagreement is due to the improper radial distribution associated with an initial microcanonical ensemble, we have also performed CTMC calculations with the initial ensemble proposed by Cohen[15] which reproduces exactly the radial distribution of $H(1s)$. The resulting probabilities are seen to extend beyond the cutoff of the microcanonical probabilities at 2 au. However, the disagreement with the B1 calculations still persists for small impact parameters. The analysis of the classical ionization probability at zero impact parameter $P(b=0)$ for different substates in $n=5$ (Fig. 5) reveals its relation to the slingshot effect and to the classical position-momentum correlation. The ionization probabilities are multiplied by the scaled impact energy in order to identify a E^{-1} dependence at high impact energies observed quantum mechanically for all substates. This dependence should not be confused with the dependence of the cross sections at high impact energies which results from the integration of the ionization probability over all impact parameters.

FIGURE 5. Total ionization probability times the scaled impact energy En^2 as function of the scaled impact energy for $p + H(n = 5, \ell, m)$ collisions at an impact parameter $b \simeq 0$: first Born approximation (full curves); CTMC method (dotted curves). The numbers in the figure indicate the quantum numbers (ℓ, m) specifying the initial state of the electron within the level $n = 5$.

Depending on the shape and orientation of the classical orbits associated with the initial state of the electron, we find that ionization can be, within the CTMC approach, either classically enhanced or classically suppressed relative to the corresponding quantal $B1$ result. For the $5s$ state the ionization probability is drastically enhanced and decreases with increasing energy only as $(E)^{-1/2}$. This counterintuitive result is a direct result of the unphysical dominance of the $\vec{p} \cdot \Delta \vec{p}$ term of the energy transfer by the slingshot. s states corresponding to orbits with eccentricities close to 1 feature segments of the orbits close to the nucleus with large local $|p(\vec{r})| \rightarrow \infty$ as $r \rightarrow 0$. Zero-impact collisions remain therefore effective in ionization despite decreasing Δp with increasing collision energy E . This artifact is a direct consequence of the strong classical $r - p$ correlation which is absent in quantum mechanics (Eqs. (25,26)). The opposite trend can be observed for the state $\ell = n - 1 = 4$ and $m = 4$, i.e. for circular orbits with the orbital plane perpendicular to the beam axis. Classical ionization is strongly suppressed compared to quantum ionization. The reason is two-fold: the electron does not experience a close encounter with the projectile at zero impact and therefore the collision approaches the distant- collision (dipole allowed) limit. Moreover, the residual

classical momentum transfer $\Delta\vec{p}$ becomes at high speeds perpendicular to the local momentum of the circular orbit thereby switching off the dominant “slingshot” contribution. An interesting intermediate case arises for $\ell = 4$, $m = 0$, i.e. for circular orbits lying in the scattering plane. In this case, close encounters between the projectile and electron are still possible for zero-impact collisions, however, $\Delta\vec{p}$ is orthogonal to $\vec{p}(\vec{r})$ at high speeds. The coupling term $\Delta\vec{p} \cdot \vec{p}$ in Eq.(17) therefore vanishes, resulting in the correct quantum mechanical energy dependence of $P_{n\ell}(0)$. The coefficient of proportionality is, however, different.

It is worth noting that, unlike the exact classical CTMC method approximate classical models such as the Thomson model do not contain the slingshot term $\sim \vec{p} \cdot \Delta\vec{p}$. Remarkably, it is this additional, unjustified approximation which has lead, coincidentally, to early successes in the description of ionization and of the stopping power [22] in agreement with quantum theory. Equally remarkable, the term $\sim \vec{p} \cdot \Delta\vec{p}$ is also responsible for the failure of exact classical calculations for charge transfer from the ground state at high energies [23,24]. This shortcoming appears to be even more surprising in view of the fact the wellknown high energy limit of electron capture cross section, $\sigma \sim v^{-11}$ results from double scattering (second-order) contribution which was discovered by Thomas [25] within the framework of classical mechanics. In his original work, Thomas neglected the initial momentum distribution of the captured electron, (i.e., $\vec{p}(\vec{r}) = 0$), and hence, the slingshot term $\sim \vec{p} \cdot \Delta\vec{p}$. In exact classical calculations it is precisely this term which gives rise to the first-order OBK-like [26] contribution to electron capture at high energies which relies on matching of the velocity between the projectile and the orbital speed. Because of the strong momentum-position correlation in the classical dynamics, electrons at small distances near the nucleus ($r \rightarrow 0$) provide strong momentum matching ($p(r) \rightarrow \infty$) for arbitrarily high speeds. Consequently, in exact classical calculations the OBK (or velocity matching) contribution overshadows the true classical Thomas double scattering contribution and gives an unrealistically large cross section at high energies. However, for electron capture from circular Rydberg states this contribution is reduced. This leads to an improved agreement with the experiment found in a recent CTMC calculation for circular Rydberg states [27].

6. Angular Distribution of Ejected Electrons

The results of the previous sections indicate that ionization becomes classically suppressed for small momentum transfers. Thus, an improved description of the spectrum of ejected electrons in ion-atom collisions can be obtained by correcting the classical (Cl) spectrum for the quantum mechanical (QM) portion which is associated with classically suppressed ionization due to small momentum transfers [12]

$$\frac{d^2\sigma}{dE_f d\Omega} \simeq \frac{d^2\sigma^{Cl}}{dE_f d\Omega} + \frac{d^2\sigma^{QM}}{dE_f d\Omega} (q_{\min} < q < \Delta p_{cr}) \quad (28)$$

where Δp_{cr} is the critical momentum transfer q below which ionization becomes classically suppressed estimated by Eq.(28) and $q_{min} = (E_f - E_i)/v_p$. The conceptual advantage of Eq.(28) is that it combines the “best of two worlds” since the quantum corrections come from a regime where perturbation theory is expected to be valid but classical dynamics fails while the non-perturbative regime can be treated exactly, though classically.

FIGURE 6. Single differential ionization cross section as a function of the angle of the ejected electron in 70 keV and 5 MeV p + H(1s) collisions. Experiments: atomic hydrogen from Rudd et al [28,29] for atomic hydrogen (open squares) and molecular hydrogen divided by a factor two (triangles). Theoretical results: CTMC (dotted curve), CTMC plus the small momentum transfer contribution of CDW-EIS (full curve) and B1 (broken curve) [12].

One application of Eq.(28) is shown in Fig. 6 for the the singly differential cross section (SDCS) integrated over all electron energies. We compare the experimental data of Rudd et al.[28,29] with theoretical results as a function of the electron angle for 70 keV and 5 MeV p+H collisions. We display the standard CTMC results and the modified CTMC calculations corrected for the quantum contributions for small momentum transfer (Eq.(30)). At 70 keV all calculations agree with each other at forward angles whereas large discrepancies appear at backward angles. Standard CTMC results systematically underestimate the cross sections at large angles because of the lack of non-classical dipole emission channels. The important point to note is that at intermediate energy collisions (70 keV) dipole transitions do not constitute the dominant contribution to the total ionization cross section but do so only in the kinetically unfavored backward region. Therefore, classical

dynamics is able to account for the dominant contribution emitted into the forward hemisphere, and hence, to the total ionization cross section but fails at backward angles. On the other hand, at high energies (5 MeV) the failure is uniform over all angles. This is to be expected in view of the fact that the mean momentum transfer at this energy $\langle \Delta p \rangle$ is small compared to $\langle p \rangle_i$, i.e., outside of the range of validity Eq.(27). This velocity regime closely mirrors the situation of Fig. 2a for small scaled momentum transfers $\Delta p_0 \ll 1$ where the classical dynamics fails over the whole spectral range.

7. Ionization of Rydberg Atoms by Half-Cycle Pulses

Very recently, Jones et al.[6] have measured the ionization of Na Rydberg atoms by subpicosecond “half-cycle” electromagnetic pulses. The atom is subject to a strong unidirectional electrical field confined to a very short time interval, whose duration T_p is shorter than or of the order of the classical orbital period T_n , n being the effective quantum level of the atom. This regime is of considerable conceptual interest as it provides a bridge between ionization by radiation fields and collisional ionization by charged particles at high energies.

A hydrogen atom subject to a pulsed electric field is described by the Hamiltonian

$$H = \frac{p^2}{2} - \frac{1}{r} - F(t)z \quad (29)$$

where $F(t)$ denotes an external electric pulse which is directed towards the positive z -axis. Comparison between Eq. (29) and Eq. (21) shows the close connection to the “kicked” atom to which Eq.(29) converges in the impulsive limit of ultrashort pulses $T_p \ll T_n$. The corresponding “kick” or momentum transfer is given by $\Delta p = \int_{-\infty}^{\infty} F(t)dt$.

In Fig. 7 we display the data for the 10% ionization thresholds of Ref.[6] for different nd ($m=0$) states in terms of the scaled variables $T_0 = T_p/T_n$ and Δp_0 together with our classical and quantum calculations [30]. These calculations were performed for hydrogen using the fact that the quantum defect in d states of Na is very small ($\delta = 0.01$). Classical calculations were also performed for Na atoms using realistic core potentials in the electron. The quantum mechanical calculations have been performed for $n = 5$ and 10 and we display results for the regions of T_p for which convergence has been reached with the basis sizes used.

All classical and quantum calculations for 10% ionization thresholds as well as the data lie on the same universal curve in the $(\Delta p_0, T_0)$ diagram, verifying the classical-quantal correspondence for ionization by short pulses. The limiting case $T_0 \gg 1$ of this curve which is equivalent to the $F \propto n^{-4}$ dependence for static electric fields. The coefficient depends, however, on the shape of the pulse and the substate populated. In the opposite limit of ultrashort pulses ($T_0 \ll 1$) the curve approaches the asymptote $\Delta p_0 \simeq 0.54$ giving rise to a dependence $\Delta p \simeq 0.54n^{-1}$ a.u. . It is important to note that this asymptote is exact and is given by the evolution operator of the “kicked” atom (Eq.(23)), i.e. the inelastic form factor.

FIGURE 7. Scaled momentum transfer for 10% ionization threshold of $H(n, \ell = 2, m = 0)$ atoms as function of the scaled pulse duration: classical results for inverse parabolic (solid line) and rectangular (dotted line) pulses, quantum mechanical result for ionization of 10d (solid triangles) and 5d (inverted solid triangles) states by rectangular pulses, and experimental data of Ref. 6 for Na(nd) atoms (equivalent to $H(n, \ell = 2, m = 0)$ multiplied by a factor of 2.5 (open surfaces).

The almost perfect agreement between exact classical and quantum calculation appears surprising since the perturbation operator for half-cycle pulse (Eq.(29)) is formally completely equivalent to the dipole coupling to an electric field of a distant collision, for which classical dynamics seems to fail. The reason is obviously the very different strength of the perturbation, i.e. Δp can be sufficiently strong to satisfy the validity criterion for classical dynamics. From Fig.3 it follows directly that 10% ionization (i.e. an ionization probability of $P_n = 0.1$) by ultrashort pulses requires a scaled momentum transfer of $\Delta p_0 = n\Delta p \simeq 0.5$. Except for very small n , the classical criterion (Eq.(27)) is well satisfied.

Another characteristic difference between short electromagnetic pulses and fast charged particle collisions originates from the time dependence of the polarization. In a fast charged-particle collision, the time-dependent electric fields consists simultaneously of a half-cycle pulse perpendicular to the beam axis $\hat{v}_p, F_{\perp}(t)$, and a full cycle pulse parallel to $\hat{v}_p, F_{\parallel}(t)$, out of phase relative to each other in the limit $v_p \rightarrow \infty$. Even for correspondingly strong perturbations (e.g., distant collisions by multiply charged projectiles).

the longitudinal momentum transfer $\Delta p_{\parallel}$ can be small compared to $\Delta p_{\perp}$ because the two half-cycles of opposite polarity largely compensate each other. This may lead simultaneously to non-classical transitions driven by $\Delta p_{\parallel}$ and to dominant classical excitation driven by $\Delta p_{\perp}$. Future experimental and theoretical investigations of excitation and ionization by short laser pulses which can be produced with variable shape, duration, and polarity may provide an ideal tool to shed new light on the subtleties of the excitation dynamics.

8. Conclusions

Our study of classical-quantum correspondence in fast ionization by charged particles and half-cycle pulses identifies the momentum transfer during the impulsive interaction, Δp as the order parameter delineating the border between classical and quantum mechanical ionization. The critical momentum transfer Δp_{cr} between which classical mechanics fails is found to be of the order $\Delta p_{cr} \simeq n^{-3/2}$ for hydrogenic initial states corresponding to a scaled momentum $\Delta p_{0,cr} = \Delta p_{cr} \cdot n \simeq n^{-1/2}$. For smaller momentum transfers, the associated De Broglie wavelength is not sufficient to "resolve" the internal structure of the atom. Consequently, the atom interacts with the collisional perturbation as a composite system rather than in terms of a sequence of two-body collisions. The classical suppression of dipole-allowed transitions is one well known consequence of this limitation. Since a realistic ion-atom collision features a broad distribution of momentum transfers the validity of classical methods depends on the observable under consideration. The convergence to the classical limit is non-uniform and is shown to depend on the relevant region in phase space. Classical dynamics is adequate in regions in phase space when $\Delta p_0 \gtrsim n^{-1/2}$ but fails in other regions when the momentum transfer is small. The breakdown of the CTMC calculation for ionization at backward angles while providing an excellent description at forward angles (see Fig. 6), provides a beautiful illustration of this point. It is in this case easily possible to correct the CTMC method for the lack of the quantum contribution to ionization, by breaking the differential cross sections as a function of the momentum transfer down into the region above and below the critical value Δp_{cr} where quantum corrections set in. Such a method (Eq.(28)) has been shown to remedy the failure of CTMC at large emission angles.

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