On quantum–classical correspondence in classical studies of atomic processes

M J Raković[1,4]**, D R Schultz**[1]**, P C Stancil**[2] **and R K Janev**[1,3]

[1] Physics Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6372, USA
[2] Department of Physics and Astronomy, University of Georgia, Athens, GA, 30602-2451, USA
[3] Macedonian Academy of Sciences and Arts, Skopje, Macedonia

E-mail: milun@mail.phy.ornl.gov, schultz@mail.phy.ornl.gov and stancil@physast.uga.edu

Abstract
A general method for the construction of the optimum classical description of a physical process on the atomic scale is presented. The method is developed for physical systems whose quantum versions are obtained by canonical quantization of their classical counterparts and it is in principle applicable even in the case of 'low' quantum numbers. The criterion determining the optimum description was essentially based on the comparison of the quantum and classical probability distributions in terms of the canonical coordinates. The main application of the method is in classical calculations of various quantities measured in atomic collision processes.

PACS numbers: 0365S, 0270L, 0365, 3410

1. Introduction

The application of classical mechanics to atomic collision processes necessitates an appropriate implementation of the quantum–classical correspondence. In particular, any physical experiment is naturally divided into three distinct steps: preparation of the initial state of the physical system, time evolution of the system, and finally the measurement. If we accept that nonrelativistic quantum mechanics correctly describes the physical world on the atomic scale, but nevertheless wish to apply classical mechanics in practical calculations, we should establish a precise correspondence between the quantum and classical descriptions for each step in the physical process/experiment. However, in many calculations in recent years, no completely consistent way of implementing quantum–classical correspondence in the first and third steps was formulated, especially in the limit of 'low' quantum numbers where the correspondence between the classical and quantum descriptions is at least ambiguous. As for the second step, the usual approach is clear: the unitary evolution in Hilbert space corresponds to a canonical evolution in phase space, both described by the same Hamiltonian function.

[4] On leave from the Institute of Physics, University of Belgrade, PO Box 57, Belgrade 11001, Yugoslavia.

We have particularly in mind an approach known as the classical trajectory Monte Carlo (CTMC) [1, 2] method which is a technique to simulate inelastic ion–atom collisions by examining statistically the results of a classical evolution of an ensemble of projectile–target configurations chosen so as to mimic certain aspects of the corresponding quantal system. It shares a number of features with other methodologies such as molecular dynamics simulations in which quantal evolutions are approximated classically, either owing to necessity stemming from the inherent complexity of treating the system quantum mechanically or due to the assumed or apparent quantum–classical correspondence. Since CTMC and similar techniques have been broadly and successfully applied (see, for example, [3–8]) we are motivated here to seek an improved basis for optimally implementing the quantum–classical correspondence for electronic states of ions and atoms applicable to ion–atom collisions and as a fundamental underpinning.

In this paper, starting from the basic principles of quantum and classical mechanics [9], we propose a method of implementing quantum–classical correspondence in the above-mentioned first and third steps of the physical process. In formulating our method, which generalizes all previously used recipes, we had in mind (in the words of Abrines and Percival [1]) only 'plausibility arguments' and not '*a posteriori* comparison with experiment'. It is our understanding that the method presented in this paper cannot be inferred from the well known phase space representations of quantum mechanics [10] or viewed as a classical limit of quantum mechanics [11]. Rather, it follows from the simple idea of constructing the optimum classical description of the atomic (collision) processes. In other words, in our approach quantum mechanics serves as a source of accurate descriptions/data of the physical processes which are then interpreted as well as possible by the classical *theory*.

The proposed method is in principle applicable to any case (i.e. regardless of the magnitude of the quantum numbers) when the quantum description of the physical system is obtained by the canonical quantization of a given classical system. In that case, by the very quantization procedure, the canonical variables q and p are the only physical variables whose quantum–classical correspondence is always unambiguous. Therefore, in addition to possible symmetry conditions, the natural criterion for the optimum classical description is essentially based on the comparison of the quantum and classical probability distributions in terms of the canonical variables. Once the classical description is constructed, all theoretically definable quantities are, of course, functions of q and p, although some of them may not be physically meaningful (for example, simultaneous measurement of position and momentum is not possible due to the uncertainty principle). This means that in our simple method there is no need to define general correspondence between dynamical functions and self-adjoint operators in Hilbert space [10]. In addition, this means that what we call the optimum classical description will in general have worse agreement with experiment in terms of other quantities (energy, angular momentum, etc) than in terms of canonical coordinates. (For instance, the phase space distributions corresponding to atomic bound states will never have sharp binding energies.)

The plan of this paper is as follows. Section 2 is devoted to the measuring process, i.e. the quantum–classical correspondence of final states of the system, while section 3 deals with the correspondence of initial states. In section 4 the method is illustrated using some elementary examples. Section 5 contains concluding remarks.

2. Correspondence of the final states: partitioning of the Hilbert and phase space

Let us start by recalling some basic quantum and classical concepts regarding the measuring process [9]. At the end of the physical process/experiment the act of the measurement always determines in what of the available states the system is found. More precisely, the measurement

determines the values of several (or possibly only one) physical quantities. This means that to each measuring apparatus corresponds a precisely defined partition of the set of possible values of the measured physical quantities. Let S be the set of all possible values of the physical quantities measured by the given apparatus. Then

$$S = \bigcup_i S_i \tag{1}$$

where each S_i corresponds to one possible measured state of the system. For instance, if the measured quantity is energy, each S_i corresponds to a certain energy interval. Or, S_i could be the collection of certain quantum numbers: for example, (n, l) in the case of single-electron capture or excitation during an ion–atom collision. Equation (1) leads to the phase space partitioning in classical mechanics and to the Hilbert space partitioning in quantum mechanics [9]. We have

$$H = \bigoplus_i H_i \qquad \Omega = \bigcup_i \Omega_i \tag{2}$$

i.e. the Hilbert space H is partitioned into the direct sum of the linear subspaces H_i, while the phase space Ω is partitioned into the union of the disjoint subsets Ω_i.

Once the three partition equations (1) and (2) are defined, the experiment and the two theories can answer the same questions. For instance, in a typical experiment we repeat the procedure many times and measure the probability that the system is in the state S_i, $w_{\exp}(S_i) = N_i/N_{\text{tot}}$, where N_{tot} is the total number of repeated measurements and N_i is the number of events that the system was found in the state S_i. For the same probability quantum mechanics gives $w_q(S_i) = \text{tr}(\rho_f P_i)$, where P_i is the projection operator on the subspace H_i and ρ_f is the density operator describing the final state of the system. Finally, the prediction of classical mechanics is $w_{\text{cl}}(S_i) = \int_{\Omega_i} F_f(p, q) \, dp \, dq$, where $F_f(p, q)$ is the distribution function describing the final state of the system.

We assume now that the quantum mechanical description of the experiment is correct and, therefore, that the correspondence $S_i \leftrightarrow H_i$ is well defined. Then the implementation of the quantum–classical correspondence in the case of the measuring process reduces to the definition of the correspondence

$$\Omega_i \leftrightarrow H_i \tag{3}$$

i.e. to the correspondence of the partition equations (2). We shall formulate three conditions imposed on this correspondence.

Let f be (one of) the physical observable(s) measured in the experiment. Further, let f_i^{q} be the part of the quantum mechanical spectrum of f corresponding to H_i, and let f_i^{cl} be the set of all classical values of f which correspond to Ω_i. Then, the first and obvious condition imposed on equation (3) is

$$f_i^{\text{q}} \subseteq f_i^{\text{cl}}. \tag{4}$$

The second condition follows from possible symmetry properties of the Hilbert space partition, equation (2). The members in the sum, H_i, are usually invariant under time translation (evolution) generated by a certain Hamiltonian operator, or they may be invariant under transformations of some symmetry group. Then the same invariance properties are required from the members Ω_i of the phase space partition, equation (2), i.e.

$$T(H_i) \subseteq H_i \quad \text{implies} \quad T(\Omega_i) \subseteq \Omega_i \tag{5}$$

where T is a (symmetry) transformation.

The third condition imposed on equation (3) follows from the 'density of states correspondence principle' [12, 13]. To formulate this condition let us define the 'classical and quantal weights' [13], W^{cl} and W^q, corresponding to the partitions, equations (2). We set

$$W_i^q = \dim(H_i) \qquad W_i^{cl} = \int_{\Omega_i} dp\, dq \qquad (6)$$

i.e. W_i^q is simply the number of linearly independent states belonging to H_i, while W_i^{cl} is the phase space volume of the subset Ω_i. The third condition imposed on the correspondence equation (3) is then

$$W_i^{cl} = C W_i^q \qquad (7)$$

for any i, where C is a constant. This condition is obviously motivated by the understanding that in the semiclassical limit each quantum state 'occupies' the volume of phase space equal to h^N, where N is the number of degrees of freedom and h is the Planck constant. For any atomic system possessing both classical and quantal descriptions one can always define a phase space partition corresponding to a given partitioning of Hilbert space, so that the conditions, equations (4), (5) and (7), are fulfilled. However, it is obvious that these conditions do not define unique classical partitioning. Nevertheless, there are no other general conditions to be imposed which are based solely on the understanding of the measuring process. Additional conditions may only come from some '*a posteriori* comparison with experiment'.

3. Correspondence of the initial states

In experiments, the physical systems are initially prepared (i.e. their initial states are determined) by fixing the values (or ranges of values) of a finite number of physical quantities. In a complete analogy with the measurement, to any such state preparation one can associate partitions of the Hilbert and phase spaces, equation (2). This means that in both descriptions of the physical experiment/process, quantal and classical, the initial state of the system belongs to one of the members, e.g. Ω_{i_0} and H_{i_0}, of the associated partitions. In general, the initial states are not completely described by belonging to Ω_{i_0} or H_{i_0} (this is the case only if the initial state is described by a Hilbert space vector, i.e. when H_{i_0} is one-dimensional, or, correspondingly by a phase space point, i.e. when Ω_{i_0} contains only one point). The quantum mechanical description of the initial state is given by the (self-adjoint, positive) density operator ρ_{in} [9], while the classical description is given by the (positive) distribution function in phase space $f_{in}(q, p)$, which satisfy the following normalization conditions:

$$\text{Tr}\, \rho_{in} = 1 \qquad \int_{\Omega} f_{in}(q, p)\, dq\, dp = 1. \qquad (8)$$

Therefore, the implementation of the quantum–classical correspondence in the case of the initial state preparation reduces to the definition of the correspondence

$$\rho_{in} \leftrightarrow f_{in}(q, p) \qquad (9)$$

or, more precisely, to the formulation of the conditions imposed on $f_{in}(q, p)$ when ρ_{in} is given.

The first condition follows from the requirement that ρ_{in} and $f_{in}(q, p)$ belong to the corresponding members H_{i_0} and Ω_{i_0}. That ρ_{in} 'belongs to' H_{i_0} precisely means that

$$\rho_{in} P_{i_0} = P_{i_0} \rho_{in} = \rho_{in} \qquad \rho_{in} P_i = P_i \rho_{in} = 0 \qquad \text{for} \quad i \neq i_0 \qquad (10)$$

(recall that P_i is the projection operator on H_i). We now require correspondingly that $f_{in}(q, p)$ 'belongs to' Ω_{i_0} and we define that condition by

$$f_{in}(q, p) \neq 0 \qquad \text{for} \quad (q, p) \in \Omega_{i_0}$$
$$\int_{\Omega \setminus \Omega_{i_0}} f_{in}(q, p)\, dq\, dp \ll 1. \qquad (11)$$

In general, the initial state of the system is stationary under a certain Hamiltonian:

$$[H_0, \rho_{in}] = 0. \tag{12}$$

(For instance, in collision processes, H_0 describes the motion before the interaction takes place.) Therefore, the correspondence principle requires that

$$\{H_0(q, p), f_{in}(q, p)\}_{PB} = 0 \tag{13}$$

where PB stands for the Poisson bracket. If ρ_{in} possesses certain symmetry properties then there are further conditions imposed on $f_{in}(q, p)$. Assume that ρ_{in} commutes with a finite number of linearly independent observables

$$[A_i, \rho_{in}] = 0 \qquad i = 1, \dots, s. \tag{14}$$

(In the language of the theory of groups, A_i are generators of the continuous symmetry group of the initial state ρ_{in}, which is in general a subgroup of the symmetry group of the Hamiltonian H_0.) Then, again, the quantum–classical correspondence requires that

$$\{A_i(q, p), f_{in}(q, p)\}_{PB} = 0 \qquad i = 1, \dots, s. \tag{15}$$

If ρ_{in} possesses any discrete symmetry the same property should be imposed on $f_{in}(q, p)$. From condition equations (13) and (15) it follows that in the initial distribution function $f_{in}(q, p)$ not all arguments $(q_i, p_i), i = 1, \dots, N$, are independent. Indeed, these two conditions can equivalently be expressed by requiring that

$$f_{in}(q, p) = F(H_0(q, p), C_1(q, p), \dots, C_k(q, p)) \tag{16}$$

i.e. that f_{in} is a function of the energy and all independent constants of motion $C_i(q, p)$ which commute with the variables $A_i(q, p)$:

$$\begin{aligned} \{H_0(q, p), C_i(q, p)\}_{PB} &= 0 \\ \{A_j(q, p), C_i(q, p)\}_{PB} &= 0 \end{aligned} \qquad i = 1, \dots, k \quad j = 1, \dots, s. \tag{17}$$

(In the language of the theory of groups, C_i are Kasimir operators of the symmetry group of the initial state $f_{in}(q, p)$.)

To summarize, we have so far defined two conditions imposed on f_{in}. The first, equation (11), follows from the correspondence of the global structures of the phase space and the Hilbert space of the system. The second one, equation (16), follows from the requirement that the symmetry properties of f_{in} and ρ_{in} are identical. In order to define $f_{in}(q, p)$ which corresponds to a given ρ_{in}, we need to make a direct comparison of the predictions of the two descriptions regarding the measurements that can be performed on the physical system.

According to quantum mechanics one can simultaneously measure at most the set of complete variables [9]. From the set of canonically conjugate classical variables $\{q_i, p_i, i = 1, \dots, N\}$, one can form a set of N complete variables and there are 2^N possible choices. Two standard choices $\{q_i, i = 1, \dots, N\}$ and $\{p_i, i = 1, \dots, N\}$ lead, respectively, to the coordinate and momentum representations of the density operator. However, any choice of the form $\{q_{i_l}, p_{j_k}, l = 1, \dots, m; k = m + 1, \dots, N\}$, is equally possible. Let $x^I = \{x_i^I, i = 1, \dots, N\}$ be any of 2^N ($I = 1, \dots, 2^N$) such sets of complete observables and let $y^I = \{y_i^I, i = 1, \dots, N\}$ denote the set of the remaining canonical coordinates. Then, the quantum and classical probability distributions in variables x^I are given by

$$w_I^q(x^I) = \langle x^I | \rho_{in} | x^I \rangle \qquad w_I^{cl}(x^I) = \int f_{in}(x^I, y^I) \, dy^I. \tag{18}$$

We now define the degree of coincidence of the predictions of ρ_{in} and $f_{in}(q, p)$ when variables x^I are measured:

$$w_I = \left(\int \sqrt{w_I^q(x^I) w_I^{cl}(x^I)} \, dx^I \right)^2 \qquad 0 \leqslant w_I \leqslant 1. \tag{19}$$

In other words, from the standpoint of variables x^I, w_I measures how 'close' the descriptions of the physical systems given by ρ_{in} and $f_{in}(q, p)$ are. In general, the probability distributions for different sets of complete variables are independent, therefore the expression

$$w = \left(\prod_{I=1}^{M} w_I\right)^{1/M} \qquad M = 2^N \qquad 0 \leqslant w \leqslant 1 \qquad (20)$$

defines the degree of coincidence of the classical and quantum descriptions when all possible sets of complete variables, which can be chosen from the set of canonical variables, are measured. We shall refer to this quantity as the 'probability' that the quantum and classical descriptions of the physical system coincide. Now we define f_{in} as the distribution function which has the form equation (16) (where F is any non-negative continuous function), which satisfies equations (8) and (11), and which is 'closest' to ρ_{in}, i.e. which maximizes w, equation (20). In other words, the optimum classical phase space distribution is a solution of the variational problem of maximization of w, which is viewed as a nonlinear functional in the space of all non-negative continuous functions F.

Concluding this section we note that we have defined the degree of coincidence between classical and quantum descriptions of the physical system by comparing the corresponding predictions of *all* possible nonequivalent measurements of canonical coordinates which are well defined in both theories. For instance, the use of a set of canonical coordinates which mixes coordinates and momenta is perfectly acceptable in classical mechanics, but it is well known that, in general, the subsequent quantization does not yield the same quantum system. (It is interesting to note that even the use of spherical coordinates in the case of a one-particle system leads to difficulties since the classical momentum p_r conjugate to the coordinate r does not possess its quantum counterpart [14].)

4. Examples

In this section we shall illustrate our method using as examples two fundamental physical systems: the one-dimensional harmonic oscillator and a particle moving in a three-dimensional centrally symmetric potential. The second system has an important application in ion–atom collision theory, where it is often used to describe approximately the motion of the 'active' electron, in its initial and final states, in such processes as charge exchange and target excitation.

4.1. Harmonic oscillator

In this case the Hamiltonian and the corresponding quantum energy spectrum are $H = p^2/2 + q^2/2$ and $E_n = n + 1/2$, where we have used the system of units $\hbar = m = \omega = 1$.

4.1.1. Final states. If at the end of some process the measured physical quantity is energy, the appropriate partitions of the Hilbert and phase space are

$$H = \bigoplus_n H_n \qquad \Omega = \bigcup_n \Omega_n \qquad (21)$$

where H_n is the one-dimensional subspace spanned by the eigenstate $|n\rangle$. Each H_n is stationary (i.e. invariant under time evolution), therefore the same property is required from Ω_n, see equation (5). This implies that each Ω_n has the form

$$\Omega_n = \left\{q, p : E_n^{(1)} < \frac{p^2 + q^2}{2} < E_n^{(2)}\right\} \qquad (22)$$

i.e. the second formula in equation (21) is essentially the partition of the real-energy semiaxes, $E \geqslant 0$. Now, since $\dim(H_n) = 1$ and

$$W_n^{cl} = \int_{\Omega_n} dp \, dq = 2\pi \int_{\Omega_n} dE = 2\pi (E_n^{(2)} - E_n^{(1)}) \qquad (23)$$

the condition equations (7), (4) become

$$2\pi (E_n^{(2)} - E_n^{(1)}) = C \qquad E_n^{(1)} \leqslant n + 1/2 \leqslant E_n^{(2)}. \qquad (24)$$

The last equation allows a simple solution:

$$E_n^{(1)} = n \qquad E_n^{(2)} = n + 1 \qquad C = 2\pi \qquad (25)$$

and we see (since in our units $2\pi = h$) that in this partition each eigenstate $|n\rangle$ 'occupies' exactly the phase space volume equal to h.

4.1.2. Initial states. If the initial state of a process is specified by the quantum number n, its quantum description is given by the wavefunction (in this case the density operator is simply a projector $\rho_n = |n\rangle\langle n|$):

$$\langle q|n\rangle = \Psi_n(q) = \frac{\exp(-q^2/2)}{(\sqrt{\pi} \, 2^n \, n!)^{1/2}} \, \mathcal{H}_n(q) \qquad (26)$$

where $\mathcal{H}_n$ is a Hermite polynomial. The momentum representation wavefunction has the same functional form, $\langle p|n\rangle = \Psi_n(p)$, and the probability distributions in coordinate and momentum representations are given by

$$w_1^{(n)q}(q) = w_n^q(q) \qquad w_2^{(n)q}(p) = w_n^q(p) \qquad w_n^q(q) = \Psi_n(q)^2. \qquad (27)$$

Our task is to define the corresponding classical distribution function $f_n(q, p)$. It has to be positive, normalized, and stationary, i.e. the condition equations (13) and (8) require that

$$f_n(q, p) = F_n(E) \geqslant 0 \qquad E = \frac{p^2 + q^2}{2} \qquad 2\pi \int_0^\infty F_n(E) \, dE = 1 \quad (28)$$

while the condition equations (11), consistent with the phase space partition of the previous section, become

$$F_n(E) \neq 0 \qquad \text{for} \quad n < E < n + 1$$
$$2\pi \left(\int_0^n F_n(E) \, dE + \int_{n+1}^\infty F_n(E) \, dE \right) \ll 1. \qquad (29)$$

The corresponding (classical) coordinate and momentum probability distribution have the same functional form and are given by

$$w_1^{(n)cl}(q) = w_n^{cl}(q) \qquad w_2^{(n)cl}(p) = w_n^{cl}(p) \qquad w_n^{cl}(q) = \int_{-\infty}^\infty F_n((p^2 + q^2)/2) \, dp. \quad (30)$$

Finally, the degree of coincidence between the classical state $f_n(q, p)$ (generated by F_n) and the quantum state $|n\rangle$ is defined by equations (19) and (20), and reduces to

$$w_n = \left(\int_{-\infty}^\infty dq \, |\Psi_n(q)| \sqrt{\int_{-\infty}^\infty F_n((p^2 + q^2)/2) \, dp} \, \right)^2. \qquad (31)$$

In general w_n is smaller than one. However, in this simple case it is instructive to consider in a little more detail the condition that w_n actually reaches unity. It is easily shown that the formal condition $w_n = 1$ is, due to Schwartz's inequality, equivalent to the integral equation

$$\int_{-\infty}^\infty F_n(E) \, dp = \frac{\exp(-q^2)}{\sqrt{\pi} \, 2^n \, n!} \, \mathcal{H}_n(q)^2 \qquad E = \frac{p^2 + q^2}{2}. \qquad (32)$$

It appears that, if the non-negativity of F_n is not required, the solutions of the last equation exist and they coincide with the Wigner distributions corresponding to the eigenstates of the harmonic oscillator [10]:

$$F_n^{\text{W}}(E) = \frac{(-1)^n}{\pi} \exp(-2E) L_n(4E) \tag{33}$$

where L_n are Laguerre polynomials. That the Wigner distributions are obtained in this way is a consequence of the well known fact that in the case of the harmonic oscillator, the propagation of the Wigner functions (which are just phase representations of the wavefunctions and therefore propagate according to unitary Schrödinger evolution) is also generated by the classical Hamiltonian function [10]. Therefore, and this is the case only when the Hamiltonian is a quadratic form of the canonical coordinates, the stationary Wigner distributions depend on the (classical) energy only. This is, however, the necessary requirement for our classical distributions, equation (28).

Among functions (33), the one corresponding to the ground state happens to be the (only) non-negative function. Therefore, in our method, it generates the optimum classical distribution

$$F_0(E) = \frac{1}{\pi} \exp(-2E) \qquad f_0(q, p) = \frac{1}{\pi} \exp(-q^2 - p^2) \tag{34}$$

corresponding to the ground state of the harmonic oscillator. The optimum classical distributions corresponding to excited states are generated by the functions $F_n(E)$ which maximize w_n, equation (31). Instead of constructing such distributions, we shall consider here the following functions:

$$F_n(E) = \begin{cases} (2\alpha/\pi) \exp(-2\alpha) & \text{if} \quad \alpha \geqslant 0 \\ 0 & \text{otherwise} \end{cases} \qquad \alpha = E - (n - 1/2) \qquad n \geqslant 1. \tag{35}$$

These functions do not maximize w_n. Nevertheless, they will serve as a good illustration of our method. It is easily found that for them

$$\langle E \rangle_n = 2\pi \int_0^\infty E \, F_n(E) \, dE = n + 1/2 \tag{36}$$

i.e. the average energies coincide with the quantum levels, while for the probabilities w_n numerical integration of equation (31) gives

$$w_1 = 0.93 \qquad w_2 = 0.91 \qquad w_3 = 0.89 \qquad w_4 = 0.88 \qquad w_5 = 0.87\dots. \tag{37}$$

We shall compare these distributions with distributions corresponding to the classical microcanonical ensembles, which are often used in practical calculations. These are defined by
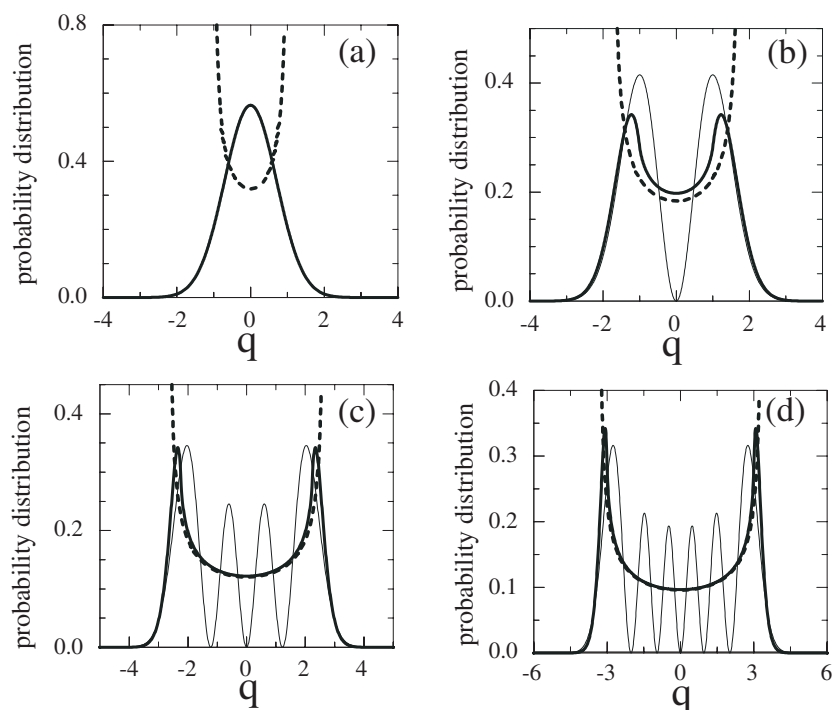
$$F_n^{\text{M}}(E) = \frac{1}{2\pi} \delta(E - n - 1/2). \tag{38}$$

This function generates the following coordinate probability distribution:

$$w_n^{\text{Mcl}}(q) = \int_{-\infty}^\infty dp \, F_n^{\text{M}}(q, p) = \begin{cases} \dfrac{1}{\pi \sqrt{2n+1-q^2}} & \text{if} \quad |q| < \sqrt{2n+1} \\ 0 & \text{otherwise} \end{cases} \tag{39}$$

and equation (31) becomes

$$w_n^{\text{M}} = \frac{4}{\pi} \left(\int_0^{\sqrt{2n+1}} dq \, \frac{|\Psi_n(q)|}{(2n+1-q^2)^{1/4}} \right)^2. \tag{40}$$

Figure 1. Probability distributions in coordinate space of the eigenstates of the harmonic oscillator for (*a*) $n = 0$, (*b*) $n = 1$, (*c*) $n = 3$ and (*d*) $n = 5$. Quantum probabilities are represented by thin solid curves, dashed ones correspond to the microcanonical ensembles, while the thick solid curves are the probabilities generated by the classical distribution functions F_n, equations (34) and (35). In the case $n = 0$ the solid curves coincide.

Numerical integration of the last formula gives

$$
\begin{aligned}
w_0^M &= 0.71 & w_1^M &= 0.73 & w_2^M &= 0.74 \\
w_3^M &= 0.75 & w_4^M &= 0.75 & w_5^M &= 0.76 \dots.
\end{aligned}
\tag{41}
$$

Note that in the semiclassical limit, i.e. as $n \to \infty$, this sequence converges (although very slowly) to one. We see that the degree of coincidence with the quantum probabilities is much greater for the phase space distributions generated by the functions F_n, equation (37), than for the microcanonical ensemble. This is also illustrated in figure 1, where the quantum probability distributions in the coordinate space of several eigenstates are compared with the corresponding classical probabilities generated by the two phase space distributions. We see that both classical distributions essentially perform averaging of the quantum oscillations, while near the turning points, where the microcanonical ensembles generate divergences, our distributions show very good agreement with the quantum predictions.

4.2. A particle in the centrally symmetric potential

In this case the Hamiltonian is defined by $H = p^2/2 + V(r)$, where atomic units $m_e = e = \hbar = 1$ are used. As already mentioned, it is often used to describe the interaction between the electron and the projectile or target in atomic collision processes.

4.2.1. Final states. If at the end of a process one measures the binding energy and angular momentum of the electron motion (for example, if one measures cross sections for capture (or excitation) into atomic states with defined quantum numbers (n, l)) the appropriate partitions of the Hilbert and the phase spaces are

$$H_{\mathrm{b}} = \bigoplus_{n,l} H_{n,l} \qquad \Omega_{\mathrm{b}} = \bigcup_{n,l} \Omega_{n,l} \qquad (42)$$

where H_{b} is the subspace of Hilbert space spanned by the bound states, while Ω_{b} is the subset of phase space containing only bound orbits. The subspaces $H_{n,l}$ are spanned by the states $|n, l, m\rangle$, $m = 0, \pm 1, \ldots, \pm l$, and their quantal weights, equation (6), are

$$W_{n,l}^{\mathrm{q}} = 2l + 1. \qquad (43)$$

Each $H_{n,l}$ is stationary and rotationally invariant and, by equation (5), the same property is required from $\Omega_{n,l}$. This is automatically achieved by constructing the partition of Ω_{b}, equation (42), via partitioning of the classical space of all possible pairs (E, L) of energy and angular momentum which correspond to the bounded motion (i.e. $E < 0$). Therefore, we shall view the second formula in equation (42) also as a partition of such space, denoted by Ω_{b}, while $\Omega_{n,l}$ will represent two-dimensional subsets of E, L space.

With this notation the condition equation (4) becomes

$$\left(E_{n,l}, \sqrt{l(l+1)} \right) \in \Omega_{n,l} \qquad (44)$$

where $E_{n,l}$ is the energy level corresponding to the quantum numbers n, l. Further, in this case the classical weights $W_{n,l}^{\mathrm{cl}} = \int_{\Omega_{n,l}} \mathrm{d}r \, \mathrm{d}p$ are equivalently expressed by

$$
\begin{aligned}
W_{n,l}^{\mathrm{cl}} &= \int_{\Omega_{n,l}} f(E, L) \, \mathrm{d}E \, \mathrm{d}L \\
f(E, L) &= 16\pi^2 L \int \frac{\mathrm{d}r}{\sqrt{2E - L^2/r^2 - 2V(r)}}
\end{aligned}
\qquad (45)
$$

where the integration in the second formula ranges over all points r for which the square root in the integrand is real. The function $f(E, L)$ can be named the classical density function in the E, L space. The condition, equation (7), now becomes

$$W_{n,l}^{\mathrm{cl}} = \int_{\Omega_{n,l}} f(E, L) \, \mathrm{d}E \, \mathrm{d}L = C(2l + 1) \qquad (46)$$

where C is a constant.

We shall now consider two particular forms of the central potential $V(r)$. In describing the interaction between an 'active' electron and the many-electron 'core' of an incompletely stripped ion, the model Green potential [15, 16]
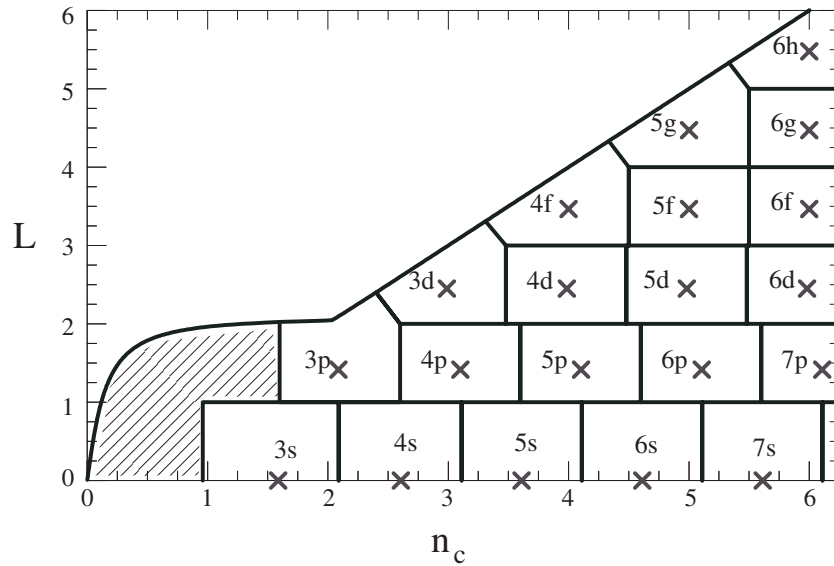
$$V(r) = \frac{(1 - \Omega(r))N_{\mathrm{e}} - Z}{r} \qquad \Omega(r) = \frac{1}{(\eta/\xi)(\exp(\xi r) - 1) + 1} \qquad (47)$$

may be adopted. Here Z is the nuclear charge, N_{e} is the number of electrons in the ionic 'core', and ξ and η are suitably chosen parameters. When $r \to \infty$

$$V(r) \to -\frac{Z_{\infty}}{r} \qquad Z_{\infty} = Z - N_{\mathrm{e}} \qquad (48)$$

and we introduce the classical action n_{c} by $E = -Z_{\infty}^2/2n_{\mathrm{c}}^2$. Instead of equation (45) we write

$$W_{n,l}^{\mathrm{cl}} = (2\pi)^3 \int_{\Omega_{n,l}} g(n_{\mathrm{c}}, L^2) \, \mathrm{d}n_{\mathrm{c}} \, \mathrm{d}L^2 \qquad (49)$$

Figure 2. A partitioning of the classical n_c, L space of the e–Na$^+$ system. The solid curve is the boundary of the space. Crosses correspond to quantum levels calculated using the Green potential. The shaded area corresponds to the phase space region inside the ionic 'core' which is already 'populated by the inner electrons'.

$$g(n_c, L^2) = \frac{Z_\infty^2}{\pi n_c^3} \int_{r_1}^{r_2} \frac{dr}{\sqrt{-Z_\infty^2/n_c^2 - L^2/r^2 - 2V(r)}} \tag{50}$$

where r_1 and r_2 are the turning points of the radial motion, and $g(n_c, L^2)$ can be considered as the density function in the classical n_c, L^2 space.

To be more concrete we shall consider the case of the sodium atom. Sodium is one of the Rydberg-like atoms, i.e. it possesses only one electron beyond the closed shells. Therefore, the interaction of the ion Na$^+$ and the outer electron is well described by the centrally symmetric potential. For that case the parameters of the Green potential are [16] $Z = 11$, $N_e = 10$, $\xi = 1.712$, $\eta = 2.85$, and the solution of the corresponding Schrödinger equation shows that the energy spectrum of the e–Na$^+$ system can be represented by a quantum defect formula $E_{n,l} = -Z_\infty^2/2(n - \delta_l)^2$, where the quantum defect δ_l is negligible for $l > 2$, and is practically independent of n. Figure 2 shows a portion of the classical n_c, L space together with the quantum levels, defined by the $(n - \delta_l, \sqrt{l(l+1)})$ pairs.

A numerical calculation of the integral in equation (50) shows that, for $n_c > 2$, the function $g(n_c, L^2)$ is negligibly different from 1. Therefore, the simple 'rectangular' partition of the phase space showed in figure 2 satisfies the desired condition equation (46). Formally, to the states not lying in the immediate vicinity of the classical n_c, L space boundary, one can assign rectangular subsets $\Omega_{n,l}$ defined by

$$\Omega_{n,l} = \{n_c, L : n - \delta_l - 0.5 < n_c < n - \delta_l + 0.5, \ l < L < l + 1\}. \tag{51}$$

The exception is the ground state 3s whose 'cell' is somewhat wider. To the states lying near the classical space boundary (3p, 3d, 4f, 5g, ...), one assigns, as shown in figure 2, suitably chosen cells using series of slanted lines whose intersections with the classical boundary are defined by the points $n_c = L = k + 1/3$, $k = 2, 3, \ldots$. Obviously the point $(n - \delta_l, \sqrt{l(l+1)})$

belongs to $\Omega_{n,l}$, while equations (49) and (50) give

$$W_{n,l}^{\text{cl}} = (2\pi)^3 (2l + 1) \tag{52}$$

i.e. the condition equation (46) is satisfied with $C = (2\pi)^3 = h^3(\text{au})$. Finally, note that the shaded area in figure 2 is not associated to any quantum state. This area obviously corresponds to the motion inside the ionic 'core', i.e. to the phase space region already 'populated by the inner electrons'.

In the case of the Coulomb interaction, $V(r) = -Z/r$, the quantum energy depends only on n, $E_n = -Z^2/2n^2$, and in that case it is meaningful to measure cross sections for capture (excitation) into states defined only by the quantum number n. Then, instead of equation (42) we have $\boldsymbol{H}_{\text{b}} = \bigoplus_n H_n$, $\boldsymbol{\Omega}_{\text{b}} = \bigcup_n \Omega_n$, and the partitioning of the classical subspace $\boldsymbol{\Omega}_{\text{b}}$ is realized via partitioning of the energy semiaxis $E < 0$. The corresponding quantal weights are

$$W_n^{\text{q}} = \sum_{l=0}^{n-1} W_{n,l}^{\text{q}} = n^2. \tag{53}$$

In this case equation (50) gives $g(n_{\text{c}}, L^2) = 1$, where as before $E = -Z^2/2n_{\text{c}}^2$. Therefore, since the boundary of the classical n_{c}, L space is the straight line $L = n_{\text{c}}$, equation (49) gives

$$W_n^{\text{cl}} = (2\pi)^3 \int_{\Omega_n} \mathrm{d}L^2 \, \mathrm{d}n_{\text{c}} = (2\pi)^3 \int_{\Omega_n} n_{\text{c}}^2 \, \mathrm{d}n_{\text{c}} = (2\pi)^3 \frac{n_2^3 - n_1^3}{3} \tag{54}$$

and $\Omega_n = [n_1, n_2]$ represents a subset of the one-dimensional classical n_{c} space containing the point n. Therefore, the condition equations (7) and (4) become

$$(2\pi)^3 \frac{n_2^3 - n_1^3}{3} = C n^2 \qquad n_1 < n < n_2. \tag{55}$$

Setting $C = (2\pi)^3 = h^3(\text{au})$ one easily constructs a solution of the last equation:

$$n_1 = [(n - 1/2)(n - 1)n]^{1/3} \qquad n_2 = [n(n + 1/2)(n + 1)]^{1/3}. \tag{56}$$

It is further possible to partition each subset Ω_n in the form $\Omega_n = \bigcup_l \Omega_{n,l}$ and to obtain the phase space partition equation (42). It is easily shown that (in the Coulomb case) the classical weights of the subsets

$$\Omega_{n,l} = \left\{ n_{\text{c}}, L : \ n_1 < n_{\text{c}} < n_2, \ \frac{l}{n} < \frac{L}{n_{\text{c}}} < \frac{l+1}{n} \right\} \tag{57}$$

are given by equation (52), and the condition equation (46) is satisfied. The above 'binning' (equation (56)) in the case of the Coulomb interaction was first proposed by Becker and MacKellar [13], and has been used in practical applications (see, for example, [17–21]). The phase space partition generated by the sets equation (57) is shown in figure 3(*a*), while figure 3(*b*) shows the 'rectangular' partition obtained for the case of the Coulomb interaction. These two partitions are continuous deformations of each other. However, the partitioning in figure 3(*a*) is characteristic of the Coulomb interaction, since in that case, the quantum spectrum is degenerate in both quantum numbers n and l. Therefore, one can choose either to partition the phase space by the subsets Ω_n, with further partitioning by $\Omega_{n,l}$ as in figure 3(*a*), or to partition the phase space by the subsets Ω_l, with further partitioning by $\Omega_{n,l}$, as is essentially done in the partitionings in figure 3(*b*) and figure 2.
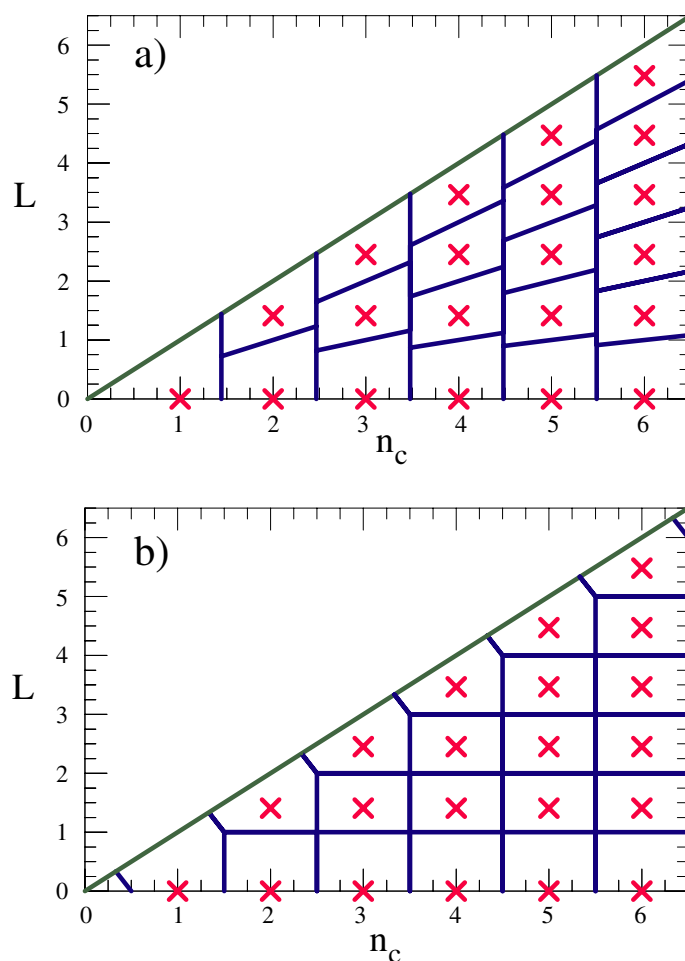
Figure 3. Partitionings of the classical n_c, L space of the hydrogen atom: (*a*) Becker–MacKellar partitioning defined by equation (57). (*b*) Rectangular partitioning; the subsets corresponding to the states not lying near the space boundary are defined by $\Omega_{n,l} = \{n_c, L : n - 1/2 < n_c < n + 1/2, l < L < l + 1\}$. The points $(k + 1/3, k + 1/3)$, $k = 0, 1, 2, \ldots$, are the intersections of the space boundary and the slanted lines used to define the subsets lying near the boundary.

4.2.2. Initial state. The initial state of the electron is usually defined by specifying the initial quantum numbers (n_0, l_0). Therefore, we shall assume that the relevant partitions of the Hilbert and phase spaces, equation (42), are defined. The quantum description of the initial state is given by the density operator

$$\rho_{\text{in}} = \frac{1}{2l_0 + 1} \sum_{m=-l_0}^{l_0} |n_0, l_0, m\rangle \langle n_0, l_0, m| \tag{58}$$

which is rotationally invariant. As a consequence its diagonal elements, i.e. the probability distributions, equation (18), in coordinate and momentum representations are also rotationally invariant:

$$w_1^{\text{q}}(\boldsymbol{r}) = \langle \boldsymbol{r}|\rho_{\text{in}}|\boldsymbol{r}\rangle = \rho_1(r) \qquad w_8^{\text{q}}(\boldsymbol{r}) = \langle \boldsymbol{p}|\rho_{\text{in}}|\boldsymbol{p}\rangle = \rho_8(p). \tag{59}$$

As explained in the previous section, these probability distributions correspond only to two out of $2^3 = 8$ possible representations, i.e. choices for the set of complete variables. Due to the rotational symmetry of ρ_{in}, the remaining six quantum probability distributions possess cylindrical symmetry and are expressed in terms of only two independent functions, ρ_2 and ρ_5:

$$
\begin{aligned}
w_2^{\text{q}}(x, y, p_z) &= \langle xyp_z|\rho_{\text{in}}|xyp_z\rangle = \rho_2\left(\sqrt{x^2 + y^2}, p_z\right) \\
w_3^{\text{q}}(x, p_y, z) &= \rho_2\left(\sqrt{x^2 + z^2}, p_y\right) \qquad w_4^{\text{q}}(p_x, y, z) = \rho_2\left(\sqrt{y^2 + z^2}, p_x\right) \\
w_5^{\text{q}}(x, p_y, p_z) &= \langle xp_yp_z|\rho_{\text{in}}|xp_yp_z\rangle = \rho_5\left(x, \sqrt{p_y^2 + p_z^2}\right) \\
w_6^{\text{q}}(p_x, y, p_z) &= \rho_5\left(y, \sqrt{p_x^2 + p_z^2}\right) \qquad w_7^{\text{q}}(p_x, p_y, z) = \rho_5\left(z, \sqrt{p_x^2 + p_y^2}\right).
\end{aligned}
\tag{60}
$$

Our task is to define the corresponding classical distribution function $f_{\text{in}}(\boldsymbol{r}, \boldsymbol{p})$. It has to be stationary and rotationally invariant, i.e. the condition equation (16) requires that

$$
f_{\text{in}}(\boldsymbol{r}, \boldsymbol{p}) = F(E(\boldsymbol{r}, \boldsymbol{p}), L(\boldsymbol{r}, \boldsymbol{p})) \qquad E = \frac{p^2}{2} + V(r) \qquad L = \sqrt{p^2 r^2 - (\boldsymbol{p} \cdot \boldsymbol{r})^2}. \tag{61}
$$

The above function generates the following probability distribution in the classical E, L space (see previous section):

$$
w_{\text{in}}^{\text{cl}}(E, L) = 16\pi^2 L \, F(E, L) \int \frac{\mathrm{d}r}{\sqrt{2E - L^2/r^2 - 2V(r)}}. \tag{62}
$$

The integration is performed over all points r for which the square root in the integrand is real. The normalization condition is

$$
\int_{\Omega_{\text{b}}} w_{\text{in}}^{\text{cl}}(E, L) \, \mathrm{d}E \, \mathrm{d}L = 1 \tag{63}
$$

and Ω_{b} is the subset of the E, L space which corresponds to the bound orbits. The condition that $f_{\text{in}}(\boldsymbol{r}, \boldsymbol{p})$ 'belongs' to $\Omega_{n_0 l_0}$, equation (11), is expressed by

$$
\begin{aligned}
w_{\text{in}}^{\text{cl}}(E, L) &\neq 0 \qquad \text{for} \quad (E, L) \in \Omega_{n_0 l_0} \\
\int_{\Omega_{\text{b}} \backslash \Omega_{n_0 l_0}} w_{\text{in}}^{\text{cl}}(E, L) \, \mathrm{d}E \, \mathrm{d}L &\ll 1
\end{aligned}
\tag{64}
$$

where $\Omega_{n_0 l_0}$ is the subset of Ω_{b} associated to the quantum numbers (n_0, l_0) in the partition equation (42).

Finally, $f_{\text{in}}(\boldsymbol{r}, \boldsymbol{p})$, equation (61), generates classical probability distributions in various sets of complete (quantum) variables, see equation (18). As in the quantum case, the probability distributions in coordinate and momentum representations are rotationally invariant, i.e.

$$
w_1^{\text{cl}}(\boldsymbol{r}) = \int F(E, L) \, \mathrm{d}\boldsymbol{p} = f_1(r) \qquad w_8^{\text{cl}}(\boldsymbol{p}) = \int F(E, L) \, \mathrm{d}\boldsymbol{r} = f_8(p) \tag{65}
$$

while the remaining six probability distributions are cylindrically symmetric and expressed in terms of the two independent functions, f_2 and f_5:

$$
\begin{aligned}
w_2^{\text{cl}}(x, y, p_z) &= \int F(E, L) \, \mathrm{d}p_x \, \mathrm{d}p_y \, \mathrm{d}z = f_2\left(\sqrt{x^2 + y^2}, p_z\right) \\
w_3^{\text{cl}}(x, p_y, z) &= f_2\left(\sqrt{x^2 + z^2}, p_y\right) \qquad w_4^{\text{cl}}(p_x, y, z) = f_2\left(\sqrt{y^2 + z^2}, p_x\right) \\
w_5^{\text{cl}}(x, p_y, p_z) &= \int F(E, L) \, \mathrm{d}p_x \, \mathrm{d}y \, \mathrm{d}z = f_5\left(x, \sqrt{p_y^2 + p_z^2}\right) \\
w_6^{\text{cl}}(p_x, y, p_z) &= f_5\left(y, \sqrt{p_x^2 + p_z^2}\right) \qquad w_7^{\text{cl}}(p_x, p_y, z) = f_5\left(z, \sqrt{p_x^2 + p_y^2}\right).
\end{aligned}
\tag{66}
$$

In the above formulae $E = p^2/2 + V(r)$ and $L = \sqrt{p^2 r^2 - (\mathbf{p} \cdot \mathbf{r})^2}$. Now, the probability that ρ_{in} and $f_{\text{in}}(q, p)$ describe the same physical system, equation (20), is given by

$$w = (w_1 w_2^3 w_5^3 w_8)^{1/8} \tag{67}$$

where, from equations (19) and equations (59), (60), (65) and (66), it follows that

$$w_1 = \left(4\pi \int_0^\infty \sqrt{f_1(r)\rho_1(r)}\, r^2 \, \mathrm{d}r \right)^2 \qquad w_8 = \left(4\pi \int_0^\infty \sqrt{f_8(p)\rho_8(p)}\, p^2 \, \mathrm{d}p \right)^2$$

$$w_2 = \left(2\pi \int_0^\infty \rho \mathrm{d}\rho \int_{-\infty}^\infty \mathrm{d}p \, \sqrt{f_2(\rho, p)\rho_2(\rho, p)} \right)^2 \tag{68}$$

$$w_5 = \left(2\pi \int_0^\infty p \, \mathrm{d}p \int_{-\infty}^\infty \mathrm{d}z \, \sqrt{f_5(z, p)\rho_5(z, p)} \right)^2.$$

Now, we define the classical phase space distribution which describes the system defined by the quantum numbers (n_0, l_0) (more precisely with the density operator equation (58)) as the one which has the form equation (61), satisfies the condition equation (64), and maximizes the probability w, equation (67). In other words, it is a solution of the variational problem of maximization of w, which is viewed as a functional in the space of all non-negative continuous functions $F(E, L)$. In general it is a difficult problem to solve, and in practical applications it may be satisfactory to maximize w in the narrower, reasonably chosen, variational space of trial functions $F(E, L)$.

In many practical applications of the CTMC method, a popular choice for the initial distribution was a microcanonical ensemble for which $f_{\text{in}} \sim \delta(H(\mathbf{r}, \mathbf{p}) - E_{n_0, l_0})$ [2, 12]. In that case, the set of phase space points for which the distribution function does not vanish is of measure zero in the phase space, and it obviously does not satisfy the first of the conditions in equation (64). With such a choice for the initial distribution, the majority of the phase space points are excluded in the descriptions of the initial states while each point necessarily belongs to some final state.

As mentioned above, when maximizing the probability w, one might be compelled to narrow down the class of trial functions F to reasons of practicality. Another possibility is to try to construct a reasonable classical distribution by solving the easier task of maximizing not w, but some of the partial probabilities w_i. For example, it was shown ([22] and references therein) that the maximization of w_1 defines a very good classical description of the ground state of the hydrogen atom. The phase space distribution defined in this way is in some sense opposite to the microcanonical ensemble which maximizes w_8. However, in general, such an approach cannot give reasonable results (indeed one can easily construct very different phase space distributions which define the same probability distrubtions in one of the sets of complete variables).

We shall conclude this section by considering the simple but important case when ρ_{in} describes the ground state of the hydrogen atom. Then

$$\rho_1(r) = \frac{\exp(-2r)}{\pi} \qquad \rho_8(p) = \frac{8}{\pi^2 (p^2 + 1)^4}$$

$$\rho_2(\rho, p_z) = \frac{2}{\pi^2} \frac{\rho^2}{1 + p_z^2} K_1^2 \left(\rho\sqrt{1 + p_z^2} \right) \tag{69}$$

$$\rho_5(z, p) = \frac{(1 + |z|\sqrt{1 + p^2})^2}{\pi(1 + p^2)^3} \exp\left(-2|z|\sqrt{1 + p^2} \right).$$

where K_1 is the Bessel function. As in the previous section, it is convenient to use instead of energy E the classical action n_c defined by $E = -1/2n_c^2$. We shall also introduce the scaled angular momentum by $\tilde{L} = L/n_c$. Then, if we adopt the phase space partition given in

equation (57), the classical n_c, $\tilde{L}$ space denoted by Ω_b and its subset Ω_{10} corresponding to the initial state with $n = 1$, $l = 0$, are

$$\Omega_b = \{(n_c, L) : \ 0 < n_c < \infty, \ 0 \leqslant \tilde{L} \leqslant 1\}$$
$$\Omega_{10} = \{(n_c, \tilde{L}) : \ 0 < n_c < 3^{1/3}, \ 0 \leqslant \tilde{L} \leqslant 1\}. \tag{70}$$

The classical distribution function takes the form $f_{in}(\boldsymbol{r}, \boldsymbol{p}) = F(n_c, \tilde{L})$ and the probability distribution in the classical n_c, $\tilde{L}$ space (see the previous section) becomes

$$w_{in}^{cl}(n_c, \tilde{L}) = 16\pi^3 n_c^2 \tilde{L} \ F(n_c, \tilde{L}). \tag{71}$$

As mentioned above, the maximization of the 'probability' w, equation (67), is hard to achieve in practical calculations, so we now define a smaller class of trial functions F. Since $n = 1$ and $l = 0$, we set

$$F(n_c, \tilde{L}) = \frac{(1 - \tilde{L}^2)^a}{C(a, b)} \exp(-b(n_c - 1)^2) \tag{72}$$

where C is a normalization constant, and a and b are to be seen as variational parameters. Note that after this choice of function F the variables n_c and $\tilde{L}$ are statistically independent. From the normalization condition, equation (63), it follows that

$$C(a, b) = \frac{8\pi^3}{a + 1} \int_0^\infty n_c^2 \exp(-b(n_c - 1)^2) \, dn_c \tag{73}$$

while the second condition in equation (64) requires that

$$\int_{3^{1/3}}^\infty n_c^2 \exp(-b(n_c - 1)^2) \, dn_c \ll \int_0^\infty n_c^2 \exp(-b(n_c - 1)^2) \, dn_c. \tag{74}$$

Finally, the substitution of equations (69), (72), (66) and (68) into (67) defines a function $w(a, b)$. Numerical calculation shows that this function reaches the maximum of $w = 0.935$ (partial probabilities being $w_1 = 0.996$, $w_2 = 0.918$, $w_5 = 0.918$ and $w_8 = 0.977$) for $a = 0$ and $b = 10.1$, i.e. these parameter values give the optimal classical distribution in the form (72).

As in the case of the harmonic oscillator, we shall compare this distribution with the one corresponding to the microcanonical ensemble which is defined by

$$F^M(E, L) = \frac{1}{(2\pi)^3} \delta(E + 1/2). \tag{75}$$

With this function the four independent probability distributions, equations (66), are easily calculated:

$$f_1^M(r) = \begin{cases} \dfrac{1}{2\pi^2} \sqrt{\dfrac{2}{r} - 1} & \text{if} \quad r \leqslant 2 \\ 0 & \text{otherwise} \end{cases} \qquad f_8^M(p) = \frac{8}{\pi^2(p^2 + 1)^4}$$

$$f_2^M(\rho, p_z) = \begin{cases} \dfrac{1}{2\pi^2} \sqrt{\dfrac{4}{(1 + p_z^2)^2} - \rho^2} & \text{if} \quad \rho \leqslant \dfrac{2}{1 + p_z^2} \\ 0 & \text{otherwise} \end{cases} \tag{76}$$

$$f_5^M(z, p) = \begin{cases} \dfrac{3}{2\pi^2} \dfrac{(1 + \frac{2}{3}a)\sqrt{a(1 - a)} + \frac{1}{2}\arccos(2a - 1)}{(1 + p^2)^{5/2}} & \text{if} \quad a = |z|\dfrac{1 + p^2}{2} \leqslant 1 \\ 0 & \text{otherwise.} \end{cases}$$

It is interesting that in this case the momentum probability distribution f_8^M coincides with the quantum one, see equation (69), i.e. $w_8^M = 1$. This is one of the reasons why this distribution is often used in practical calculations. However, the numerical calculations show that in this case
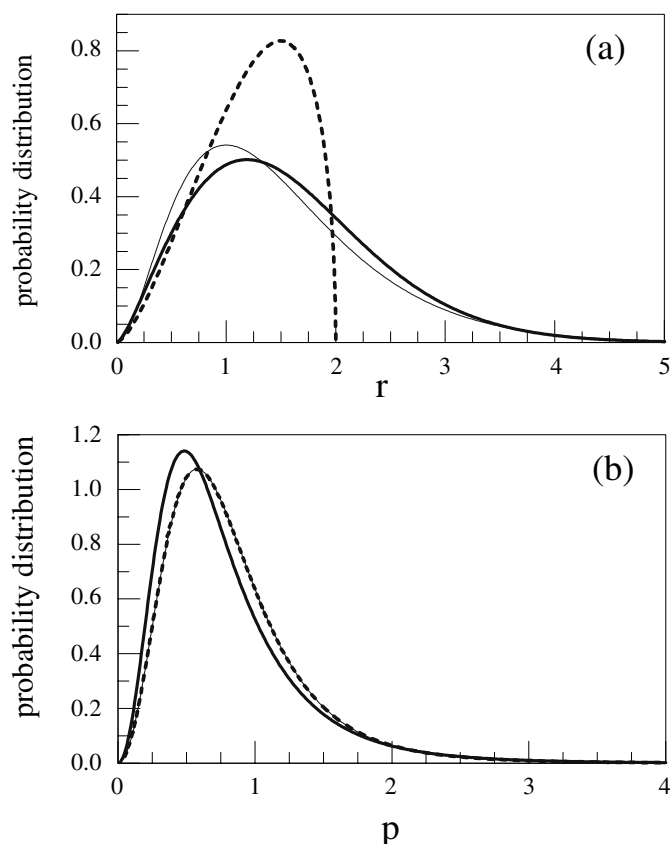
Figure 4. Probability distributions in (*a*) coordinate and (*b*) momentum space for the ground state of the hydrogen atom. Quantum probabilities are represented by thin solid curves, dashed ones correspond to the microcanonical ensembles, while the thick solid curves are the probabilities generated by the classical distribution function F, equation (72), with $a = 0$, $b = 10.1$. In plot (*b*) the thin solid and dashed curves coincide.

the total degree of coincidence with the quantum state is $w^M = 0.800$ (partial probabillities being $w_1^M = 0.740$, $w_2^M = 0.736$, $w_5^M = 0.828$ and $w_8^M = 1$), i.e. it is much smaller than in the case of the distribution in the form (72). To illustrate this, figure 4 compares the probability distributions in coordinate and momentum representations generated by these two classical phase space distributions with the corresponding quantum probabilities.

5. Concluding remarks

In this paper we have presented a fairly general method for the construction of the optimum classical description of a physical process on the atomic scale. The method is not the consequence of any classical or semiclassical limit of quantum mechanics, and it is not related to known phase space representations of quantum mechanics. Our method is developed for physical systems whose quantum versions are obtained by the canonical quantization of their classical counterparts, and it is in principle applicable even in the case of 'low' quantum numbers. The criterion for the optimum description was essentially based on the comparison of the quantum and classical probability distributions in terms of the canonical coordinates.

The main application of the method is in classical calculations of various quantities measured in atomic collision processes.

As a look forward toward other work, we note that a very unorthodox improvement of the method would be a possible modification of the 'second step' of the physical process, i.e. evolution. In one of the quasiclassical methods applied to atomic collision processes, the Wigner phase space distributions are used for the representation of the initial and final states of the system but the evolution, in the zeroth approximation, is realized by canonical transformation generated by the classical Hamiltonian function [10]. Higher corrections are obtained by using noncanonical time evolution (in fact the exact evolution is just the phase space representation of the unitary evolution). Analogously, in our method one might try to modify the Hamiltonian function describing the evolution so that better agreement with experiment is reached. For example, in applying classical mechanics to the description of the helium atom seen as a three-body system, one might try to modify the interaction potential (for example, somehow remove the Coulomb singularity) so that the stable bound states are classically possible. Of course, the change in the potential will inevitably introduce modifications: for example, in the quantum spectrum of the hydrogen atom. However, if these modifications are of the order of other well known corrections to the Coulomb spectrum the modified interaction potential might prove useful.

Acknowledgments

References

[1] Abrines R and Percival I C 1966 *Proc. Phys. Soc.* **88** 873
[2] Olson R E and Salop A 1977 *Phys. Rev.* A **16** 531
[3] Olson R E 1981 *Phys. Rev.* A **24** 1726
[4] Olson R E, Ullrich J and Schmidt-Böcking H 1989 *Phys. Rev.* A **39** 5572
[5] Schultz D R, Olson R E, Reinhold C O, Kelbch S, Kelbch C, Schmidt-Böcking H and Ullrich J 1990 *J. Phys. B: At. Mol. Opt. Phys.* **23** 3839
[6] Schultz D R, Meng L and Olson R E 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** 4601
[7] Schultz D R and Reinhold C O 1994 *Phys. Rev.* A **50** 2390
[8] Kerby G W, Gealy M W, Hsu Y-Y, Rudd M E, Schultz D R and Reinhold C O 1995 *Phys. Rev.* A **51** 2256
[9] Jauch J M 1968 *Foundations of Quantum Mechanics* (Reading, MA: Addison-Wesley)
[10] Lee H-W 1995 *Phys. Rep.* **259** 147
[11] Zhang W-M and Feng D H 1995 *Phys. Rep.* **252** 1
[12] Percival I C and Richards D 1975 *Advances in Atomic and Molecular Physics* vol 11, ed D R Bates (New York: Academic)
[13] Becker R L and MacKellar A D 1984 *J. Phys. B: At. Mol. Phys.* **17** 3923
[14] Messiah A 1965 *Quantum Mechanics* (Amsterdam: North-Holland)
[15] Garvey R H, Jackman C H and Green A E S 1975 *Phys. Rev.* A **12** 1144
[16] Schultz D R and Reinhold C O 1998 *Comput. Phys. Commun.* **114** 342
[17] Olson R E and Schultz D R 1989 *Phys. Scr.* T **28** 71
[18] Meng L, Reinhold C O and Olson R E 1989 *Phys. Rev.* A **40** 3637
 Meng L, Reinhold C O and Olson R E 1990 *Phys. Rev.* A **42** 5286
[19] Schultz D R, Meng L, Reinhold C O and Olson R E 1991 *Phys. Scr.* T **37** 89
[20] Schultz D R and Krstic P S 1995 *Atomic and Plasma-Material Interaction Data for Fusion* **5** 173
[21] Schultz D R, Krstic P S and Reinhold C O 1996 *Phys. Scr.* T **62** 69
[22] Schultz D R, Reinhold C O, Olson R E and Seely D G 1992 *Phys. Rev.* A **46** 275