Exact Wave Functions for the Coulomb Problem from Classical Orbits

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We present a simple formula that expresses energy eigenfunctions for the Coulomb problem exactly and entirely in terms of the corresponding classical orbits. Since both energy eigenvalues and eigenfunctions can be obtained exactly by a semiclassical procedure, the full quantum dynamics of the electron in a Coulomb field can be expressed completely in terms of its classical motion.

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The relationship between the classical orbits and the observed behavior of the hydrogen atom was a central issue in the old quantum theory [1] and has remained a subject of fascination for nearly a century. Modern interest in this topic [2–4] can, in part, be attributed to the continuing desire to attain a more thorough understanding of the quantum-classical correspondence and develop new, accurate, semiclassical approximations. However, much of the attention that has been focused on the classical aspects of the Coulombic problem in the past few years can be traced to the recent observation of wave packet recurrences in high-n Rydberg atoms [5] that strongly suggest motion of the electron in classical Kepler orbits. These experiments have stimulated several theoretical attempts to identify Coulombic coherent states that evolve in a manner most closely resembling the classical dynamics [4].

In this paper, we show that a special and very deep relationship exists between the classical and the quantum behavior of an electron in a Coulomb field. In particular, we demonstrate that the energy eigenfunctions for such a system can be expressed exactly and entirely in terms of the corresponding classical electron motion. As a consequence, the quantum dynamical evolution of the electron in a Coulomb field can, in principle, be completely described by classical mechanics.

The above property is similar to one that has been known for some time to apply to the case of the harmonic oscillator (HO) [6]. To proceed, it will be useful to review the exact classical expression for HO wave functions in a generalized context. We thus consider a multidimensional system with f degrees of freedom. An (generally approximate) expression for the wave function describing a state with quantum numbers $\mathbf{n} = (n_1, \dots, n_f)$ is given by [7]

$$\Psi_{\mathbf{n}}(\mathbf{q}') = \mathcal{N} \int c e^{i\phi/\hbar} e^{iw/\hbar}\, d\boldsymbol{\alpha}\,, \tag{1}$$

where the integral is taken over the f-dimensional Lagrangian manifold associated with quantized actions $\mathbf{J} = (\mathbf{n} + \boldsymbol{\delta}/4)\hbar$, the δ_i being the Maslov indices. This manifold is parametrized by the angle variables $\boldsymbol{\alpha}$ conjugate to the $\mathbf{J}$. In the above expression,

$$\phi = \mathbf{p}^T(\mathbf{q}' - \mathbf{q}) + i(\mathbf{q}' - \mathbf{q})^T \boldsymbol{\Gamma} (\mathbf{q}' - \mathbf{q})\,, \tag{2}$$

where $q_i(\boldsymbol{\alpha})$ and $p_i(\boldsymbol{\alpha})$ are the Cartesian coordinates and conjugate momentum variables on the Lagrangian manifold, $\boldsymbol{\Gamma}(\boldsymbol{\alpha})$ is an $f \times f$ complex symmetric matrix, periodic in the angle variables, and having a positive definite real part, and

$$w = \int^{\mathbf{q}} \mathbf{p}^T\, d\mathbf{q} \tag{3}$$

is Hamilton's characteristic function (the time-independent action integral). The lower limit of the integral in Eq. (3) is arbitrary since it only affects the overall phase of the wave function. The preexponential factor c in Eq. (1) is given by

$$c = [\det(\mathbf{P} - 2i\boldsymbol{\Gamma}\mathbf{Q})]^{1/2}, \tag{4}$$

where

$$(\mathbf{P})_{ij} = \frac{\partial p_i}{\partial \alpha_j}\,, \qquad (\mathbf{Q})_{ij} = \frac{\partial q_i}{\partial \alpha_j}\,, \qquad i,j = 1, \dots, f\,, \tag{5}$$

are stability matrix elements. Finally, $\mathcal{N}$ is a normalization constant.

For the particular case of a HO with potential $V(\mathbf{q}) = \sum_{i=1}^{f} (\mu_i \omega_i^2 q_i^2)/2$, Eq. (1) becomes an exact expression for the wave function provided that $\boldsymbol{\Gamma}$ is chosen to be diagonal with elements $\Gamma_{ii} = \mu_i \omega_i / 2$ [6]. Although Eq. (1) does not remain exact for more general systems, a stationary phase treatment shows that this expression (with arbitrary admissible $\boldsymbol{\Gamma}$) nevertheless reduces to the Wentzel-Kramers-Brillouin (WKB) formula for the wave function in the classical limit. Equation (1) is, thus, a semiclassical asymptotic formula. Additionally, it can be shown that Eq. (1) is actually superior to the WKB formula as a semiclassical approximation since it provides a globally uniform semiclassical treatment for states that occupy regular regions of phase space [7]. From this perspective, Eq. (1) is a uniform semiclassical expression that becomes exact for the special case of the HO.

Equation (1) has an appealing physical interpretation. A Gaussian coherent state function $\exp(i\phi/\hbar)$ is centered on the classical particle as it travels along each trajectory that semiclassically corresponds to the quantum state $\mathbf{n}$ of interest. Each such function is weighted by the preexponential factor c and multiplied by the ubiquitous semiclassical

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phase factor $\exp(iw/\hbar)$. The resulting functions then add together coherently at each point $\mathbf{q}'$ to form the wave function for the system.

We now present an expression analogous to Eq. (1) that describes the energy eigenstates for the Coulomb problem. Focusing on the bound states of the hydrogen atom for specificity, the wave functions are given by

$$\Psi_{nlm}(\mathbf{r}') = \mathcal{N} \int C e^{i\Phi/\hbar} e^{iW/\hbar}\, d\boldsymbol{\alpha}\,, \tag{6}$$

where the integral is over the three-dimensional Lagrangian manifold associated with the quantized values of the action variables for the desired state:

$$N = n\hbar, \qquad L = (l + 1/2)\hbar, \qquad M = m\hbar\,. \tag{7}$$

This manifold is parametrized by the angle variables $\boldsymbol{\alpha} = (\alpha_N, \alpha_L, \alpha_M)$, conjugate to (N, L, M), which take on values in the range $(0, 2\pi)$. Other quantities appearing in Eq. (6) are

$$\Phi = \mathbf{p}\cdot(\mathbf{r}' - \mathbf{r}) + (p_r r + iL)(r'r - \mathbf{r}'\cdot\mathbf{r})/r^2, \tag{8}$$

where (r', θ', φ') and (r, θ, φ) are, respectively, the spherical components of $\mathbf{r}'$ and $\mathbf{r}(\boldsymbol{\alpha})$, and $(p_r, p_\theta, p_\varphi)$ are the spherical components of the momentum $\mathbf{p}(\boldsymbol{\alpha})$ conjugate to $\mathbf{r}$. In addition,

$$W = \int^{r} p_r\, dr + \int^{\theta} p_\theta\, d\theta + \int^{\varphi} p_\varphi\, d\varphi \tag{9}$$

is Hamilton's characteristic function; the preexponential factor is given by $C = C_r C_\theta$, where

$$C_r^2 = [L/r^2 + i(\partial p_r/\partial r)_{\alpha_L,\alpha_M}]p_r/r^2, \tag{10}$$

$$C_\theta^2 = L\cos\theta - ip_\theta \sin\theta\,, \tag{11}$$

and $\mathcal{N}$ is again a normalization constant.

Equation (6) is perhaps most easily verified by explicitly evaluating the integrals over $\boldsymbol{\alpha}$. Here we sketch only the steps involved. Further details will be presented elsewhere.

The angular components of $\mathbf{r}$ and $\mathbf{p}$ and the function W must be expressed in terms of the variables α_L, α_M, L, and M. The necessary transformations can be found in many references [1,8]. This yields

$$\Psi_{nlm}(\mathbf{r}') = \mathcal{N}' \int d\boldsymbol{\alpha}\, C_r e^{i\Phi_r/\hbar} e^{iW_r/\hbar} \times e^{(r'/r)Ge^{-i(\alpha_L+\psi)}} e^{il(\alpha_L+\psi)+im\alpha_M}, \tag{12}$$

where

$$\Phi_r = p_r(r' - r) + iLr'/r\,, \tag{13}$$

$$W_r = \int^{r} p_r\, dr\,, \tag{14}$$

$$G = \sqrt{L^2 - M^2}\cos\theta' + i[L\sin(\alpha_M - \varphi') + iM\cos(\alpha_M - \varphi')]\sin\theta', \tag{15}$$

$$\psi = \int^{r} (\partial p_r/\partial L)\, dr\,, \tag{16}$$

and $\mathcal{N}'$ is a constant. It is most convenient to perform the integration over α_L in Eq. (12) first. Expanding the exponential factor involving G in Eq. (12) in a power series and changing the integration variable to $\alpha_L + \psi$ immediately gives

$$\Psi_{nlm}(\mathbf{r}') = \mathcal{N}' R(r') \frac{2\pi}{l!\,\hbar^l} e^{im\varphi'} \int_0^{2\pi} G^l e^{im(\alpha_M - \varphi')}\, d\alpha_M\,, \tag{17}$$

where

$$R(r') = \int_0^{2\pi} C_r (r'/r)^l e^{i\Phi_r/\hbar} e^{iW_r/\hbar}\, d\alpha_N\,. \tag{18}$$

Changing the integration variable in Eq. (17) to $\tau = \alpha_M - \varphi'$ and expanding G^l in powers of $\exp(i\tau)$ yields a finite power series in the variable $(\tan\theta'^2)$ that, apart from a constant factor, can be recognized as a standard expression for the associated Legendre function $P_l^m(\cos\theta')$ [9].

The remaining factor $R(r')$ can now be evaluated by expressing r, p_r, and W_r in terms of action N and the variable u, defined by the condition $\alpha_N = u - \epsilon\sin u$, where $\epsilon = (1 - L^2/N^2)^{1/2}$. By changing the integration variable to

$$z = -\left(\frac{2r'}{na_0}\right)\frac{e^{-iu}}{e^{-iu} - v}\,, \tag{19}$$

where a_0 is the Bohr radius and $v = [(N + L)/(N - L)]^{1/2}$, and comparing the resulting integral to a known representation of the Laguerre function [10], $R(r')$ is shown to be equal to the exact (but unnormalized) radial factor of the hydrogenic atom.

The net result is that Eqs. (6) and (18), respectively, express the three-dimensional wave function and the radial factor for bound states of the hydrogen atom exactly in terms of the classical motion of the electron. Actually, these expressions continue to be valid for unbound (continuum, positive energy) states of the atom and for the repulsive Coulomb interaction (Rutherford scattering). In such cases, the radial motion is not quantized, α_N is replaced by a timelike variable with infinite limits, and it can be shown that $R(r')$ can be expressed in terms of the appropriate Coulomb wave function.

The similarity of Eqs. (6) and (18) to Eq. (1) suggests that the present functions $\exp(i\Phi/\hbar)$ and $\exp(i\Phi_r/\hbar)$ should be interpreted as generalizations of the Gaussian coherent state functions $\exp(i\phi/\hbar)$ appearing in the first treatment. Analogously, the present functions can be viewed as traveling with the electron along its classical trajectories and coherently adding together to build the wave function. The deviations of $\exp(i\Phi/\hbar)$ and $\exp(i\Phi_r/\hbar)$ from the Gaussian form are evidently necessary to ensure that the new expressions correctly incorporate the effect of the Coulomb singularity and properly treat the boundary condition for $R(r')$ at $r' = 0$, so that they yield the desired, exact results for the Coulomb problem.

An additional relationship between our Coulomb expressions and Eq. (1) can be seen if Φ and Φ_r are expanded to second order in $(\mathbf{r}' - \mathbf{r})$ and $(r' - r)$, respectively. It can then be shown that $\Psi_{nlm}(\mathbf{r}')$ and $R(r')$ take on the precise form given by Eq. (1) for the cases $f = 3$ (and nondiagonal $\mathbf{\Gamma}$) and $f = 1$, respectively. This result immediately allows us to apply a stationary phase treatment to show that the expressions in Eqs. (6) and (18) approach WKB forms in the classical limit, even for non-Coulombic potentials. Thus, in analogy to the case of the HO, the new expressions are semiclassical formulas that may be applied for a variety of potentials but that have the special property of becoming exact only for the Coulomb potential.

An even stronger relationship between the HO and Coulombic wave functions is revealed by replacing Φ with $\Phi + i\gamma(r' - r)^2$ and C_r^2 with $C_r^2 + 2\gamma$ in Eqs. (6) and (10), where $\gamma = (L - irp_r)/(2r^2)$. The factor $\exp(i\Phi/\hbar)$ then becomes the Gaussian coherent state function $\exp[i\mathbf{p} \cdot (\mathbf{r}' - \mathbf{r})/\hbar - \gamma|\mathbf{r}' - \mathbf{r}|^2/\hbar]$ and, after a bit of work, the revised Eq. (6) can be shown to be an exact expression for the wave function of the three-dimensional isotropic HO in the state (n, l, m). The classical expressions for the wave functions of the Coulombic system and the three-dimensional HO are, thus, very similar. It is not yet clear whether this similarity can be simply explained as a consequence of the known relationship [11] between the wave functions for the hydrogen atom and the four-dimensional HO.

The above remarks help explain the origins of our classical expression for the Coulombic wave function. Equation (6) was obtained from the classical wave function for the three-dimensional isotropic HO by removing the quadratic term $i\gamma(r' - r)^2$ from Φ and correcting C accordingly. This step was guided by the expectation that the classical wave functions for the two systems should be similar (e.g., due to the known similarity of the radial functions) but that expressions for hydrogenic wave functions should not involve Gaussian factors in r'. The isotropic HO wave functions were, in turn, obtained by casting Eq. (1) in terms of spherical variables. Throughout, formation of the integrands was guided by the requirement that they reduce to the form of Eq. (1) when Φ is expanded to second order, thus ensuring the proper classical limit for the wave functions.

The analogy between the HO and Coulombic cases leads one to expect the function $\exp(i\Phi/\hbar)$ in Eq. (6) to conform to one of the existing definitions [4] of a Coulombic coherent state. However, this does not appear to be the case. In fact, $\exp(i\Phi/\hbar)$ does not even obey the basic condition of quadratic integrability as a function of $\mathbf{r}'$ that is implicit in the current definitions. Nevertheless, it is interesting that the corresponding factor $(r'/r)^l \exp(i\Phi_r/\hbar)$ appearing in the radial function $R(r')$ is closely related to Nieto's minimum uncertainty coherent state [12] for the radial Coulomb problem. The relationship of the present treatment to existing forms of Coulombic coherent states deserves further study.

To summarize, we have presented an exact and remarkably simple formula that expresses the energy eigenstates of an electron in a Coulombic field in terms of the corresponding classical orbits. It has been previously established that semiclassical treatments of this system are capable of yielding exact bound state energy eigenvalues [13], residues of the momentum space Green function (sums of n^2 products of bound energy eigenfunctions) [14], and scattering amplitudes [15]. The present work shows that an appropriate semiclassical treatment of this system gives exact individual energy eigenfunctions as well. The Coulomb problem thus joins the harmonic oscillator as a special system having wave functions that can be completely described in terms of classical quantities. Clearly, if a classical treatment can determine both the eigenvalues and a complete set of eigenstates exactly, it can also describe the system's time dependence exactly. Thus, the dynamics of the Coulomb system can be fully described in terms of its ordinary, real, classical orbits.

It is not difficult to extract from the results presented here exact classical expressions for the energy eigenstates for the rigid rotor and the radial wave functions for the isotropic HO. These, together with exact classical wave functions for a number of other simple systems will be presented elsewhere.

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