RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 56, NUMBER 1 JULY 1997

Semiclassical formula for oscillator strengths in atomic spectra

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(Received 3 March 1997)

A simple semiclassical formula is given for the oscillator strengths of high Rydberg states of a hydrogen atom in an electric field. The oscillator strength of a state is proportional to the square of the function representing the quantum angular distribution of outgoing waves, evaluated at the classical angle of ejection from the atom that sends the electron into a semiclassically quantized eigentrajectory. The formula gives an interpretation of the envelopes of Stark manifolds in photoabsorption spectra; it is in good agreement with quantum calculations. The formula may also be used for other integrable or near-integrable systems.
[S1050-2947(97)50407-0]

PACS number(s): 32.60.+i

INTRODUCTION

Semiclassical approximations are widely used for calculation of excited energy levels. The standard modern framework is the Einstein-Brillouin-Keller-Marcus (EBKM) torus quantization method [1]. It is easy to use, it has been widely applied, and it is known to give accurate energy levels for excited states ''in the limit $\hbar \rightarrow 0$.'' However, it does not so easily give other properties of quantum states. For example, the calculation of oscillator strengths requires much more work, and the accuracy of the results is less certain. In this paper we develop a simple expression for oscillator strengths for a hydrogen atom in an electric field, and we show by comparison with quantum calculations that the formula is accurate.

I. TORUS QUANTIZATION

The EBKM theory is also known as the (corrected) Bohr-Sommerfeld quantization scheme, or as ''torus quantization.'' The method begins from the presumption that, for the system of interest, classical dynamics is integrable. If there exists a canonical transformation from the original phase-space coordinates $(\mathbf{p},\mathbf{q})$ to action-angle variables $(\mathbf{I},\boldsymbol{\phi})$, then the classical trajectories foliate phase-space as a family of tori. Each torus is labeled by the values of the action variables, $\mathbf{I}$, and the motion on each torus is quasiperiodic.

From this continuous family of tori, we pick out a particular discrete set, the ''eigentori,'' or ''eigentrajectories'' (Fig. 1). These are the tori that have appropriately quantized values of action variables

$$\mathbf{I}=(\mathbf{n}+\boldsymbol{\lambda}/4)\hbar, \tag{1}$$

where $\mathbf{n}$ is a vector of integers, and $\boldsymbol{\lambda}$ is the vector of Maslov indices (in our case $\boldsymbol{\lambda}=2$). The energies of the eigentori

$$H(\mathbf{I})=H((\mathbf{n}+\boldsymbol{\lambda}/4)\hbar) \tag{2}$$

are approximations to the quantum energy levels of the system.

II. OSCILLATOR STRENGTHS

The oscillator strength density $Df(E)$ from a specified initial state $\mathbf{i}$ is defined as

$$Df(E)=\sum_{\mathbf{n}} f_{\mathbf{n}}^{\mathbf{i}}\delta(E-E_{\mathbf{n}}), \tag{3}$$

where $f_{\mathbf{n}}^{\mathbf{i}}$ is the oscillator strength for the transition from state $\mathbf{i}$ to state $\mathbf{n}$,

$$f_{\mathbf{n}}^{\mathbf{i}}=2|\langle \psi_{\mathbf{n}}|D|\psi_{\mathbf{i}}\rangle|^2(E_{\mathbf{n}}-E_{\mathbf{i}}), \tag{4}$$

where D is the relevant component of the dipole operator.

The EBKM method can be used to calculate approximate wave functions, and therefore to calculate all other observable properties of an atomic system; in particular, it can be used to calculate oscillator strengths. Some effort might be

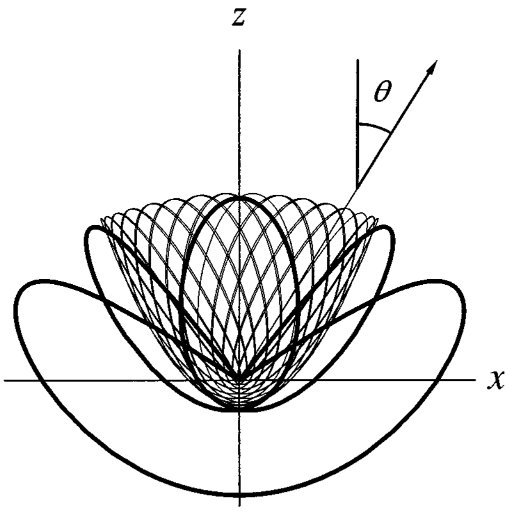

FIG. 1. Three trajectories of an electron in the final state with $m=0$ (arbitrary units). The external electric field is directed along the z axis. Bold lines show two closed trajectories with the ratio of periods equal to 1/2 and 2/3. Their shapes depend only on scaled energy $\epsilon=E/F^{1/2}$, and are shown for $\epsilon=-1$. The thin line is a part of the eigentrajectory for $n_1=35$ and $n_2=3$ in an external field of 282.39 V/cm. This trajectory corresponds to the ejection eigenangle $\Theta=31.46°$. It is quasiperiodic, not necessarily closed at the origin.

required, however. Primitive semiclassical wave functions diverge at caustics and foci, and they have to be repaired; also one typically needs some integral of the wave function to calculate the desired quantity (such as oscillator strength). From such integrals it may be difficult or impossible to extract simple analytical expressions, and the accuracy of such expressions may be unknown. In contrast, quantum methods are often easy to automate, and they give accurate numbers, but they might not give much physical insight.

III. CLOSED-ORBIT THEORY

A quite different semiclassical method is the periodic-orbit theory of Gutzwiller [2] and its application to atomic spectra, which is called closed-orbit theory [3]. This theory is especially useful for calculating the large-scale structure of the absorption spectrum of an atom in applied electric and/or magnetic fields. This theory gives a simple formula for the average oscillator strength density:

$$Df(E)=Df_0(E)+\sum_k C_k(E)\sin\Delta_k(E). \tag{5}$$

Here $Df(E)$ is the same quantity as in Eq. (3). $Df_0(E)$ is the ‘‘background absorption’’—the oscillator strength density that would be present if the electron directly escaped from the atom and never returned. The sum is over all closed orbits, including repetitions. A closed orbit is a path of the electron that begins and ends at the nucleus (Fig. 1). $\Delta_k(E)$ is equal to the classical action $S_k(E)=\oint \mathbf{p}\cdot d\mathbf{q}$ around the closed orbit, plus certain corrections associated with Maslov indices. $C_k(E)$ is a quantity we call the recurrence amplitude. In atomic units it is equal to [4]

$$C_k(E)=C(E-E_i)\sin\Theta_k|Y(\Theta_k)|^2B_k. \tag{6}$$

For this paper, the important quantity is $|Y(\Theta_k)|^2$. Here Θ_k is the ejection angle and the return angle of the kth closed orbit (for a hydrogen atom in an electric field, the orbit returns to the nucleus from the same direction that it went out). $Y(\Theta)$ is the angular distribution of outgoing waves as calculated from quantum mechanics. If there were no external fields applied to the atom, and if the laser were tuned to such a frequency as to produce outgoing electrons with total energy equal to zero, then the resulting wave function would be the Green's function acting on the dipole function times the initial state

$$G^{+}_{E=0}D|\psi_i\rangle=C_1[\exp(i\sqrt{8r})/r^{3/4}]Y(\theta,\varphi), \tag{7}$$

with $Y(\theta,\varphi)$ being the angular distribution of these waves [4]. For example, if $m_l=0$ in the initial and final states,

$$Y(\theta)=\sum_l(-1)^l b_l^i I(n_i,l_i,l)Y_{l,0}(\theta,0), \tag{8}$$

where b_l^i is a Clebsch-Gordan coefficient, and $I(n_i,l_i,l)$ is a radial dipole integral between the initial state (n_i,l_i) and the regular zero-energy Coulomb radial wave function,

$$I(n_i,l_i,l)=\int_0^\infty R_l^{0,\mathrm{reg}}(r)R_{n_i,l_i}(r)r^3dr. \tag{9}$$

For example, if the initial state is $s\ \ (l=0)$, and the radiation is z polarized, then $Y(\theta)$ is a constant times $\cos\theta$. Finally, B_k is the classical amplitude for the closed orbit,

$$B_k=r_0^{-1/4}|\partial\theta_f/\partial\theta_i|^{1/2}, \tag{10}$$

which is related to the divergence of neighbors from the central closed orbit. Additional details are in Ref. [3].

IV. CONNECTION

There must be a correspondence between Eqs. (3) and (5), since they both represent the same observable quantity. For the density of states, Berry and Tabor [5] established the correspondence between Gutzwiller's periodic-orbit formula and the EBKM formula. We have recently derived the corresponding connection between Eqs. (3) and (5) for the oscillator strength density. The derivation is long, and the details will be published in the future. Here we report that we obtained from this connection a simple semiclassical formula for oscillator strengths of individual levels, $f_{\mathbf{n}}^{\mathbf{i}}$. The derivation and the formula apply to general integrable and near-integrable systems. Below we consider the case of a hydrogen atom in a uniform electric field.

V. HYDROGEN IN AN ELECTRIC FIELD

The Hamiltonian is

$$H=p^2/2-1/r+Fz=E. \tag{11}$$

Azimuthal motion is ignorable (we take $L_z=0$), and the variables are separable using semiparabolic coordinates

$$\begin{aligned} u&=(r+z)^{1/2}=r^{1/2}\cos(\theta/2),\\ v&=(r-z)^{1/2}=r^{1/2}\sin(\theta/2). \end{aligned} \tag{12}$$

Using also a scaled time τ defined such that $dt/d\tau=r$, the effective Hamiltonian becomes $\mathcal{H}=H_u+H_v$, where

$$\begin{aligned} H_u&=p_u^2/2-Eu^2+Fu^4/2=1+\beta,\\ H_v&=p_v^2/2-Ev^2-Fv^4/2=1-\beta. \end{aligned} \tag{13}$$

In the Schrödinger equation we replace p_u^2 by $(u^{-1}\partial_u u\partial_u)$, and similarly for p_v^2. β is the separation constant, and has the range $-1\leqslant\beta\leqslant1$. From Eqs. (13) it follows that each state is labeled by two parabolic quantum numbers $\mathbf{n}=(n_1,n_2)$ corresponding to the two action variables (I_u,I_v), which are quantized as

$$\begin{aligned} I_u(E,\beta)&=(1/\pi)\int_0^{u_0}\sqrt{2(1+\beta+Eu^2)-Fu^4}\,du\\ &=(n_1+1/2)\hbar,\\ I_v(E,\beta)&=(1/\pi)\int_0^{v_0}\sqrt{2(1-\beta+Ev^2)+Fv^4}\,dv\\ &=(n_2+1/2)\hbar, \end{aligned} \tag{14}$$

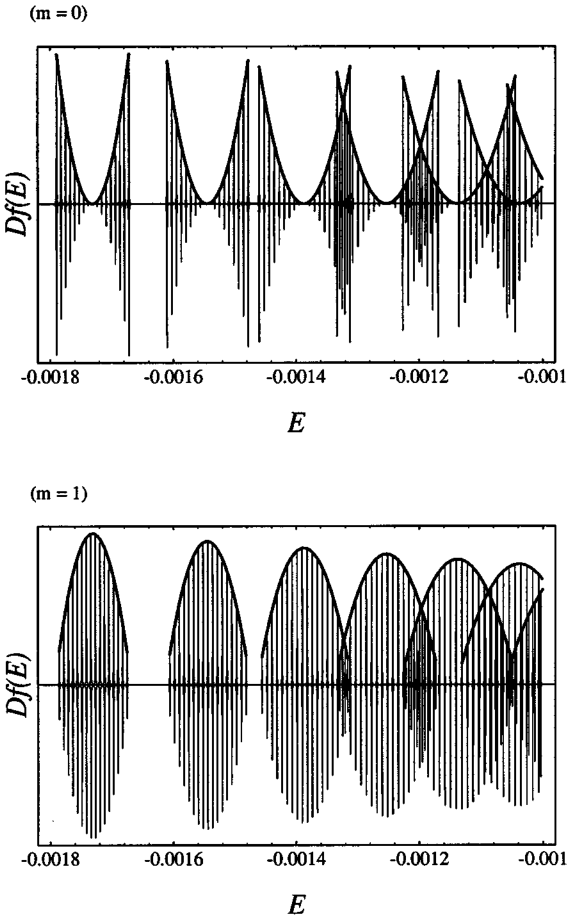

FIG. 2. Photoexcitation spectrum from the $1s$ state of a hydrogen atom to Stark manifolds $n=17$ to 23 (energy in hartrees; oscillator strength is dimensionless). For these plots, the absorption lines were artificially widened. The semiclassical formula (15) (upper part of graphs) is compared to a quantum calculation (lower part of graphs); the latter was provided to us by Robicheaux. Light is polarized parallel to $(m=0)$ or perpendicular to $(m=1)$ the electric field. The bold lines are the envelopes of Stark manifolds. These envelopes repeatedly show the shape of the angular distribution of electrons ejected from the atom as explained in Fig. 3.

where (u_0,v_0) are the turning points of the u or v motions (first zero of the integrand). These quantization conditions imply that both the energy E and the separation constant β are quantized.

The separation constant β has an important physical meaning. If we set $\beta_{\mathbf{n}}= \cos\Theta_{\mathbf{n}}$, then $\Theta_{\mathbf{n}}$ is the angle at which the **n**th eigentrajectory intersects the origin (Fig. 1). Each eigentrajectory not only has a characteristic energy, but also a characteristic angle, which we call the ''ejection angle'': electrons going out from the nucleus in the direction $\Theta_{\mathbf{n}}$ with energy $E_{\mathbf{n}}$ find themselves on the **n**th eigentorus [6].

VI. SEMICLASSICAL FORMULA FOR OSCILLATOR STRENGTH

The formula for the oscillator strength of each state is

$$f_{\mathbf{n}}^{\mathbf{i}}=R|Y(\Theta_{\mathbf{n}})|^2, \tag{15}$$

$$R=(8\pi)(E_{\mathbf{n}}-E_{\mathbf{i}})|\partial(E,\beta)/\partial(I_u,I_v)|. \tag{16}$$

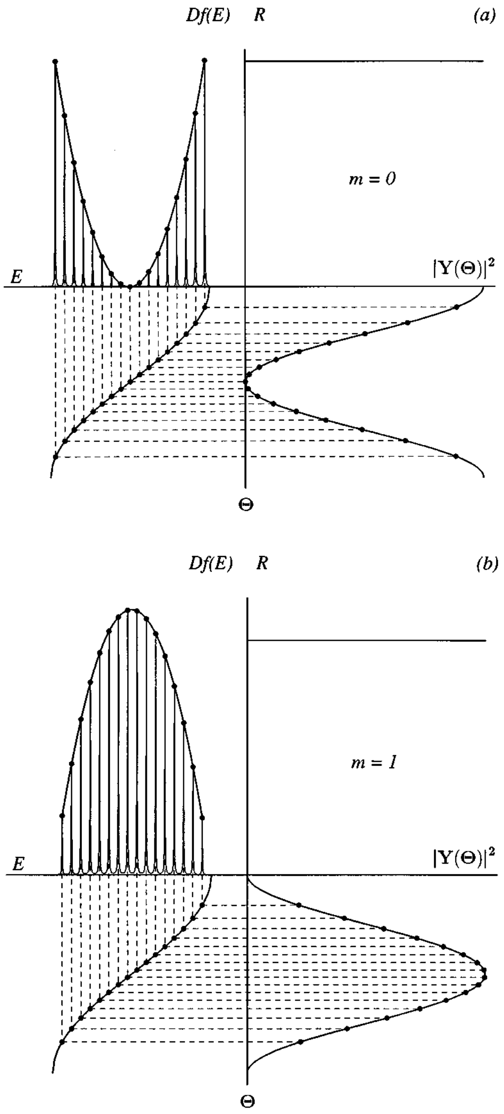

FIG. 3. Combined plot showing the semiclassical interpretation of the envelopes of spectral lines in the photoabsorption spectra in an external electric field. Presented is the case of photoexcitation from the $1s$ initial state of a hydrogen atom by the laser field (a) polarized parallel to the external field axis, which populates the final states with $m=0$ and (b) polarized perpendicularly, which populates the final states with $m=1$. Starting from the upper right part of plot (clockwise): (1) The factor R [Eq. (16)] plotted against the values of $|Y(\theta)|^2$ is almost constant within a manifold. (2) The graph of the angular distribution $|Y(\theta)|^2$, which is $\cos^2\theta$ in case (a) and $\sin^2\theta$ in case (b). (3) The dependence of the ejection angle Θ on energy within a Stark manifold; the bullets show the ejection eigenvalues $\Theta_{n_1,n_2,m}$ vs eigenenergies $E_{n_1,n_2,m}$. (4) The resulting absorption spectrum—the oscillator strength density $Df(E)$ as a function of energy, with the envelope that essentially mimics the shape of the angular distribution $|Y(\theta)|^2$.

The oscillator strength is proportional to the angular distribution of outgoing waves at the ejection angle of the **n**th eigentorus. It also contains the Jacobian of the transformation from the conserved quantities E and β to action variables (I_u,I_v); this we have found to be a slowly varying factor.

Let us examine the consequences of this formula before explaining it more fully. In first order, the energy levels, the separation constant, and the ejection angle are given by the formulas [7],

$$E=-1/(2n^2)+(3/2)n(n_1-n_2)F, \tag{17}$$

$$\beta=\cos\theta=(n_1-n_2)(-2E)^{1/2}, \tag{18}$$

$$E=-1/(2n^2)+(3/2)n^2F\cos\Theta. \tag{19}$$

Here n is the principal quantum number $(n=n_1+n_2+m+1)$ and m is the magnetic quantum number. [In all of our calculations we show the exact numerical solutions to the semiclassical equations (14); the qualitative behavior is understood from the first-order equations (17)–(19).]

In Fig. 2 we show Stark manifolds for $m=0$ and $m=1$ with the principal quantum number n varying from 17 to 23. The lower manifolds are separated, but the higher ones start to overlap. Also in Fig. 2 our semiclassical formula (15) is compared with a quantum calculation, kindly provided for us by Robicheaux. Note that in each manifold the oscillator strengths show a characteristic shape—a hill for $m=1$ or a valley for $m=0$.

This shape is a ‘‘map’’ of the angular distribution $|Y(\theta)|^2$. Figure 3 illustrates the origin of the effect for the manifold $n=17$. In Eq. (15), the factor R is almost constant within a manifold (it is plotted in the upper right corner of Fig. 3 vs values of the angular distribution $|Y(\theta)|^2$). Therefore the shape of the envelope of the peaks is determined by the angular distribution. Its graph as a function of ejection angle θ is shown in the lower right corner of the Fig. 3. For ionization from the $1s$ initial state of hydrogen by parallel-polarized light, this is proportional to $\cos^2\theta$ [Fig. 3(a)], whereas for perpendicular polarization it is proportional to $\sin^2\theta$ [Fig. 3(b)]. (For ionization from higher states, or if spin-orbit coupling is important, the shape is more complicated.) The ejection angle θ depends monotonically on energy within the manifold [compare Eq. (19)]. In the lower left part of Fig. 3, the bullets on this graph show the correspondence between the eigenvalues of energy and those of ejection angle. (It is interesting that the extreme possible ejection angles, 0 and π, can never be the eigenvalues. For such ejection angles, the electron would stay on the field axis for an infinite time, violating the uncertainty principle. For the envelope of the absorption lines, this cuts the tails from the graph of $|Y(\theta)|^2$.) Finally, the graph of the oscillator strength density vs energy is presented in the upper left part of Fig. 3, together with its envelope. The envelope therefore is a map of the shape of the angular distribution. It is repeated in every Stark manifold (whether they overlap or not) as was seen in Fig. 2.

CONCLUSION

We give a semiclassical formula for oscillator strengths for the high Rydberg states of a hydrogen atom in an applied electric field. The formula combines three concepts. (i) Quantum: there is an angular distribution of electron waves going out from the atom under the action of a laser field. (ii) Semiclassical: each quantum state (n_1,n_2,m) corresponds to a unique classical trajectory with quantized actions. (iii) Classical: that trajectory has a unique ‘‘angle of ejection from the atom’’ $\Theta(n_1,n_2,m)$. The formula says: the oscillator strength to the (n_1,n_2,m) state is proportional to the absolute square of the quantum angular function at the quantized ejection angle, $f_{n_1,n_2,m}=\text{const}\times|Y(\Theta_{n_1,n_2,m})|^2$. This formula is tested against quantum calculations and is found to be accurate. It explains the shape of the envelope of peaks in the absorption spectra.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation and by the Office of Naval Research. We thank F. Robicheaux for the quantum calculations, and J. Shaw for suggesting them and for many helpful conversations.

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[6] Proof: From Eqs. (12), a line going out from the origin at angle θ has $u/v=\cot\theta/2$, while from Eqs. (13) near the origin $p_u/p_v=(1+\beta)/(1-\beta)=(1+\cos\theta)/(1-\cos\theta)=\cot(\theta/2)$.

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