PERIODIC ORBITS AND THE CLASSICAL-QUANTUM CORRESPONDENCE FOR DOUBLY-EXCITED STATES OF TWO-ELECTRON ATOMS [1]

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ABSTRACT

We study the classical-quantum correspondence for a collinear model of the Helium atom. The quantum spectrum of doubly-excited quasibound states is calculated using the stabilization method, and analyzed in terms of unstable classical periodic orbits using the Gutzwiller semiclassical trace formula. Oscillations in the density of states associated with modes of asymmetric stretch character are found to be prominent, whereas those due to the Wannier ridge (symmetric stretch) periodic orbit are absent.

INTRODUCTION

The Helium atom has long served as a focus for investigations of the nonseparable quantum mechanical three-body problem. There is currently much interest, both experimental and theoretical, in the properties of multiply-excited states of few-electron systems [1] "planetary atom" [2, 3]). In doubly-excited states of He and H^- in which both electrons have comparable principal quantum numbers, correlation renders traditional independent-particle descriptions

[1] Report published in Proceedings of the Adriatico Research Conference on Quantum Chaos, edited by H. A. Cerdeira, R. Ramaswamy, M. C. Gutzwiller and G. Casati, pp. 436-448, (World Scientific, 1991). This short paper, rejected by Physical Review Letters, presented the first application of Gutzwiller periodic orbit theory to the analysis of doubly-excited states of 2-electron systems. The semiclassical periodic orbit analysis of the quantum mechanical density of states for the collinear Helium model presented here provided a clear refutation of the then-prevailing dogma associating intrashell doubly-excited states with excitation of the symmetric stretch ($r_1 = r_2$) Wannier ridge mode. Further details of both the classical mechanical study of the 3-body problem and the quantum calculations mentioned in the paper are given in the unpublished Cornell Ph.D. thesis of J-H. Kim (1993). For subsequent developments, see: G. S. Ezra, K. Richter, G. Tanner and D. Wintgen, "Semiclassical cycle expansion for the Helium atom", J. Phys. B **24**, L413-L420 (1991); G. Tanner, K. Richter and J. M. Rost, "The theory of two-electron atoms: between ground state and complete fragmentation", Rev. Mod. Phys. **72**, 497-544 (2000).

inadequate, and these states have been analyzed using a variety of novel approaches [1]. Threshold laws governing the energy dependence of cross sections for two-electron ionization following electron impact or photoionization reflect the profound effects of correlation on the relative motion of slow electrons [4].

On general correspondence principle grounds, planetary atoms would appear to be good candidates for semiclassical analysis due to the large quantum numbers involved [3]. The problem of semiclassical quantization of multielectron systems was however left unsolved in the Old Quantum Theory, and the classical-quantum correspondence for few-electron systems is not fully understood even today. Although much work has been done on the semiclassical mechanics of two-electron systems [5, 6], an understanding of the nature of "ridge" states [1], associated in an as yet poorly understood sense with classically unstable motions, remains elusive. Attempts to calculate energies of doubly-excited states of He by EBK quantization of mechanical models derived from the Old Quantum Theory have not been successful [6]. Rigidly rotating configurations of the classical He atom have been found [7], but the significance of these periodic orbits for the spectrum of quasibound states is not yet clear. The well-known instability of the classical He atom with respect to autoionization makes the study of its phase space structure a difficult task.

For integrable systems, quantum energy levels can be calculated to good accuracy by imposing EBK quantization conditions on classical invariant tori [8]. Over the past few years, there have been major advances in the semiclassical theory of chaotic systems, for which invariant tori do not exist. Gutzwiller [9] has expressed the quantum density of states $n(E)$ as the sum of a smooth background term $\bar{n}(E)$ plus an oscillating term $n_{\rm osc}(E)$, where the latter is given in terms of a sum over all classical periodic orbits (pos):

$$n_{\rm osc}(E) = \sum_r \sum_j A_{rj}(E) \cos\left\{ j \left[\frac{2\pi S_r(E)}{\hbar} - \frac{\pi}{2}\alpha_r \right] \right\}. \qquad (1)$$

The index r labels the primitive pos and the index j labels repetitions of the primitive pos. $S_r(E)$ is the action of the po r divided by 2π, α_r is a generalized Maslov index, and the amplitude factor $A_{rj}(E)$ depends on the period and stability properties of the po r [9]. Eq. (1) is valid for determining the semiclassical spectrum of quasi bound autoionizing resonances as well as bound states [10].

The po theory was originally applied to calculate the lowest few eigenvalues of the anisotropic Kepler problem [9]. For large enough mass anisotropies, there are no invariant tori, and a complete symbolic coding of all (isolated, unstable) pos by periodic binary sequences is possible [9]. The slow convergence (or lack thereof) of expression (1) for real values of the energy E in

general precludes the calculation of individual eigenvalues [11]. Nevertheless, the Gutzwiller formula determines the density of states smoothed to a finite resolution ΔE in terms of a sum over all classical pos with periods up to $T \sim \hbar/\Delta E$. Undulations in calculated and observed spectra of the H-atom in a magnetic field have been interpreted quantitatively in terms of closed orbits [12, 13]; in particular, the Fourier transform of the absorption spectrum at constant scaled energy consists of a set of discrete peaks that can be put in 1:1 correspondence with classical pos [12].

THE MODEL HAMILTONIAN

We use the Gutzwiller formula to investigate the classical-quantum correspondence for doubly-excited states of a model Hamiltonian describing two electrons in the field of an infinitely heavy nucleus of charge Z,

$$H = \frac{p_1^2}{2} + \frac{p_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_1 + r_2}\,, \tag{2}$$

where $0 \leq r_1, r_2 \leq \infty$. Only the radial (stretching) degrees of freedom are included. The relative angular (bending) motion is suppressed ($\theta_{12} = \pi$), and the total angular momentum set equal to zero. This system has previously been studied classically by Watanabe [14] (also [15, 16]).

The equations of motion are singular, due to the possibility of either binary (r_1 or $r_2 \to 0$) or triple (both $r_1, r_2 \to 0$) collisions, and must be regularized for accurate trajectory integration [17]. The 3-body Coulomb potential is homogeneous of degree minus one, so that it is only necessary to study the phase space structure at one energy (strictly, at one negative, one positive, and at zero energy, where $E = 0$ corresponds to all three particles at infinite separation), as trajectories at different energies can be obtained by appropriate scaling [3]. In particular, po initial conditions, actions and periods all scale in known fashion with energy. (Oscillator systems with homogeneous potentials have been studied for just this reason [18].) If the action of po r at energy $E = -1$ is $S_r(-1)$, the action of the scaled po at negative energy E is $(-E)^{-1/2} S_r(-1)$, so that the natural energy variable is the scaled energy $\varepsilon = (-E)^{-1/2}$. The po sum for $n_{\rm osc}(\varepsilon)$ becomes

$$n_{\rm osc}(\varepsilon) = \sum_r \sum_j A_{rj}(\varepsilon) \cos\left\{ j \left[\frac{2\pi\varepsilon S_r(-1)}{\hbar} - \frac{\pi}{2}\alpha_r \right] \right\} \tag{3}$$

so that the power spectrum of the density of states $n_{\rm osc}$ will have peaks at action values $S_r(-1)$.

We have studied the classical dynamics for $Z = 2$ at energy $E = -1$. The collinear He atom is highly chaotic, and we have been unable to find any bound *quasiperiodic* trajectories (invariant tori) or stable pos. Phase points lie with unit probability on scattering trajectories,

and ionize to give $He^+ + e^-$ for $t \to \pm\infty$. (At negative total energy, double ionization is not possible.) As the classical dynamics of collinear He is essentially the same at all energies, it follows that there are no quasiperiodic trajectories corresponding to the quantum mechanical bound states (those lying below the first ionization threshold at $E = -2.0$). There exists however a measure zero set of bound trajectories, composed of isolated unstable pos, associated homoclinic and heteroclinic orbits, and bound aperiodic orbits [10]. Some pos (all unstable) for collinear He are shown in Fig. 1. The po associated with the Wannier ridge is the symmetric stretch orbit S_1 with $r_1 = r_2$ (Fig. 1(a)) This orbit begins and ends in a triple collision, and is very unstable (see below). A small asymmetric stretch component of the motion will in general result in ionization.

Enumeration of all pos and calculation of their actions, periods, and instability exponents would enable the semiclassical density of bound states or quasibound resonances to be calculated via Eq. (3), thereby achieving a semiclassical quantization of the (collinear) Helium atom. For the few chaotic systems for which this program has actually been carried through, either a complete symbolic organization of the pos has been available [9, 19] or only a small number of pos has been used [20]. It has recently been shown that a complete binary code exists for the pos of collinear He [21].

Much insight into the classical-quantum correspondence for chaotic systems has nevertheless been gained by using the Gutzwiller formula "in reverse" to interpret oscillatory structure in experimental and theoretical spectra and densities of states [12, 13, 18]. We shall follow this procedure here by analyzing the theoretical density of doubly-excited states for collinear He in terms of classical pos using the Gutzwiller formula Eq. (3). The 1-dimensional ($l = 0$) H-atom has been used as a model in the quantum mechanical theory of the microwave ionization of Rydberg states [22]. The quantum Hamiltonian for collinear He, obtained by setting

$$\frac{1}{2}p_i^2 \to -\frac{1}{2}\frac{d^2}{dr_i^2} \tag{4}$$

in Eq. (2) ($\hbar = 1$), is equivalent to that for two 1-d He ions coupled by the interelectronic repulsion, and has been diagonalized in a spatially symmetric (singlet) direct product basis of 2-electron functions formed from a complete denumerable orthonormal set of single-particle states [22]

$$\phi_n^\nu(r) = \frac{2Zr}{\nu}\left[\frac{2Z}{\nu n(n+1)}\right]^{1/2} L_{n-1}^{(2)}(\rho)e^{-\rho/2},\ n = 1, 2, \ldots, \tag{5}$$

where the scaled radius $\rho = 2Zr/\nu$. The scale parameter ν determines the character of the single-particle basis. A subset of functions $\{\phi_n^\nu, n = 1, \ldots, N > \nu\}$ is appropriate for describing single-particle states with principal quantum numbers $\sim \nu$.

To calculate the positions of highly excited quasibound doubly-excited states of collinear He, we use the stabilization method [23]. The Hamiltonian is diagonalized with a fixed basis size for a large number of values of the parameter ν, and the eigenvalues examined as a function of ν. The physically significant eigenvalues are those that are stable with respect to variation of ν. Rather than extracting individual eigenvalues directly from the stabilization graph, we produce a smoothed spectrum by superimposing the eigenvalue spectra at different ν values with a Gaussian weighting given to every eigenvalue. The stable eigenvalues associated with quasibound states then emerge as peaks above a smooth background, as seen in Fig. 2, which is obtained with a basis of 1830 functions ($N = 60$) and 400 ν values in the range 20 to 45, and covers an energy range corresponding roughly to doubly excited states (n, $n' = n$) with principal quantum number n ranging from 20 to 45.

PERIODIC ORBIT ANALYSIS OF THE DENSITY OF STATES

The power spectrum obtained by Fourier transformation with respect to ε of the segment of the smoothed quantum density of quasibound states of Fig. 2 is shown in Fig. 3, and consists of a series of sharp peaks. The action values of the peaks in Fig. 3 are listed in Table I. Each peak in the power spectrum up to $S/\hbar = 12.0$ (as far as we have gone) can be assigned to at least one primitive po or to a 2-fold repetition of a primitive po shown in Fig. 1. Peaks associated with pos symmetric with respect to $r_1 \leftrightarrow r_2$ appear at half of the action of the complete po, except for S_1 [24]. The peak with the smallest action (1.83) corresponds to the po H_1, which is a hyperangular mode [14] or "rpo" [25] involving asymmetric stretching motion of the two electrons. Other prominent peaks correspond to pos with significant asymmetric stretch character (for example, the peak at $S/\hbar = 9.06$ corresponding to the po P_2 of Fig. l(d). The action of the Wannier or symmetric stretch mode S_1 is $2 \times (Z - 0.25) = 3.50$. *There is no peak at the action of this po in Fig. 3.* Our computed approximation to the density of doubly-excited quasibound states therefore shows no oscillations associated with the po corresponding to motion along the Wannier ridge, and no evidence for sequences of doubly-excited levels described by quantization of the Wannier ridge motion [26].

We have found a number of closed orbits in addition to the ridge po S_1 that begin and end in triple collision. There are no peaks in the power spectrum corresponding to these pos.

DISCUSSION AND CONCLUSIONS

The absence of a peak corresponding to the po S_1 in the power spectrum of the density of states may be understood in terms of its instability relative to, for example, H_1. As noted by

Watanabe, H_1 is much less unstable ("quasistabl") than S_1 [14]. A quantitative measure of po instability is the characteristic exponent λ. The negligible magnitude of the peak in the power spectrum of the density of states corresponding to S_1 with respect to that corresponding to H_1 is a consequence of the exponential decrease of the amplitudes A_{rj} of Eq. (1) and (3) with λ [9]. The lack of influence of S_1 on the density of states may be understood physically in terms of the time evolution of wavepackets, initially localized at $r_1 = r_2$, launched along the pos S_1 and H_1, respectively. In the semiclassical limit, a wavepacket set off along a classical po will at short times spread at a rate determined by the corresponding classical instability exponent λ [27]. For the wavepacket set off along S_1, spreading will be very rapid and recurrences very weak, whereas that set off along H_1 will spread less rapidly and exhibit more pronounced recurrences. The rapid decay of recurrences for the wavepacket moving along the po S_1 means that the amplitude of the associated oscillations in the density of states will be small [27], whereas the stronger recurrences associated with the po H_1 imply a more pronounced influence on the density of states.

Richter and Wintgen [16] have very recently calculated λ for the Wannier mode in planar He. They find the remarkable result that the characteristic exponent of the Wannier mode S_1 in the $J = 0$ (collinear) limit is *infinite*. This fact implies that, in the semiclassical limit, oscillations associated with the Wannier po are rigorously absent from the density of states.

Further work on doubly-excited states along the lines initiated here is clearly required. In addition to detailed examination of wavefunctions for collinear He (currently in progress), our analysis must obviously be extended to 3-dimensional Helium. In this connection, it is interesting to note that the intrashell doubly-excited $(n = n')\ ^1S^e$, $v = 0$ levels tabulated by Molina [28] for $n = 3 - 6$ are fit very well by a double-Rydberg formula [28]

$$E_m = -\frac{\zeta_{\rm eff}^2}{(m-\mu)^2}, \tag{6}$$

where $\zeta_{\rm eff}$ is an effective nuclear charge, μ a two-electron quantum defect and m an integer, with $\zeta_{\rm eff} = 1.823$, $\mu = -0.0642$. The value of $\zeta_{\rm eff}$ is very close to that expected for a sequence of states with energies determined by Bohr-Sommerfeld quantization of the *unstable* hyperangular mode [29]. An analogous result also holds for H^-, where $\zeta_{\rm eff} = 0.825$ [30], while the action of the po H_1 is 0.827 [21].

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Table 1: Comparison of actions of peaks in the power spectrum of Figure 3 with those of classical unstable pos of collinear He at $E = -1$. Each peak in the power spectrum can readily be assigned to one or more primitive pos or to 2-fold repetitions of primitive pos (denoted by superscript 2).

Peak action	Periodic orbit assignment
1.83	H_1 (1.83)
3.64	H_2 (3.62), H_1^2 (3.66)
5.37	A_1 (5.40), H_3 (5.33)
7.03	A_2 (7.05), H_4 (6.97)
7.29	P_1 (7.26), H_2^2 (7.24)
8.63	A_3 (8.56), H_5 (8.57)
9.05	P_2 (9.08)
10.20	A_4 (10.22), H_6 (10.14)
10.61	P_3 (10.58), H_3^2 (10.66)
10.91	P_4 (10.91)
11.76	A_5 (11.77), H_7 (11.69)

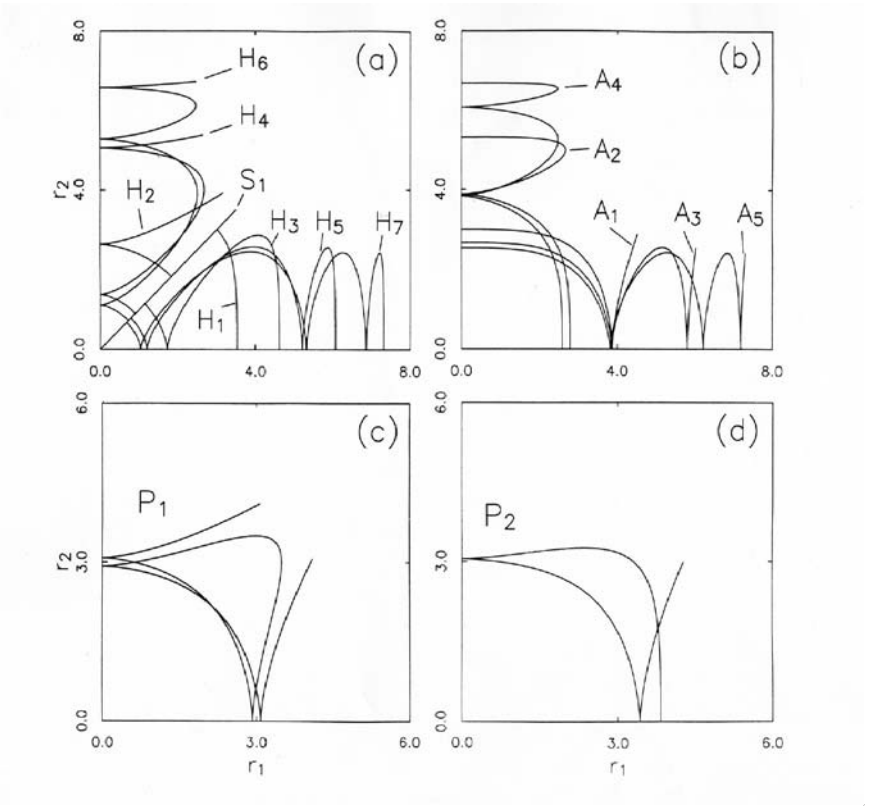

Figure 1: Periodic orbits for collinear He at $E = -1$. (a) The ridge po S_1 and the sequence H_1 – H_7. For clarity only half of each symmetrical po H_i is shown. (b) The sequence of pos A_1 – A_5. (c) The po P_1. (d) The po P_2. P_3 and P_4 (not shown) are similar in character to H_2 and P_1, respectively.

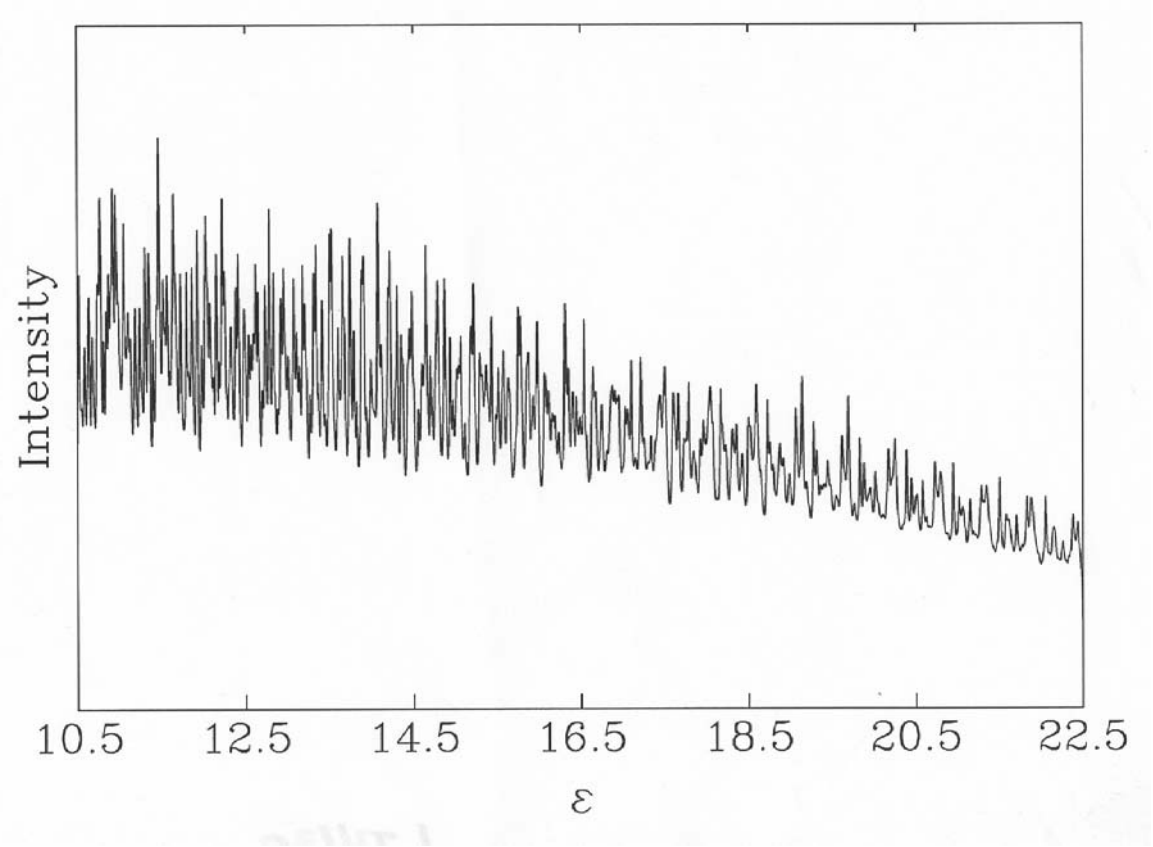

Figure 2: The smoothed approximate quantum density of quasibound states obtained using the stabilization method.

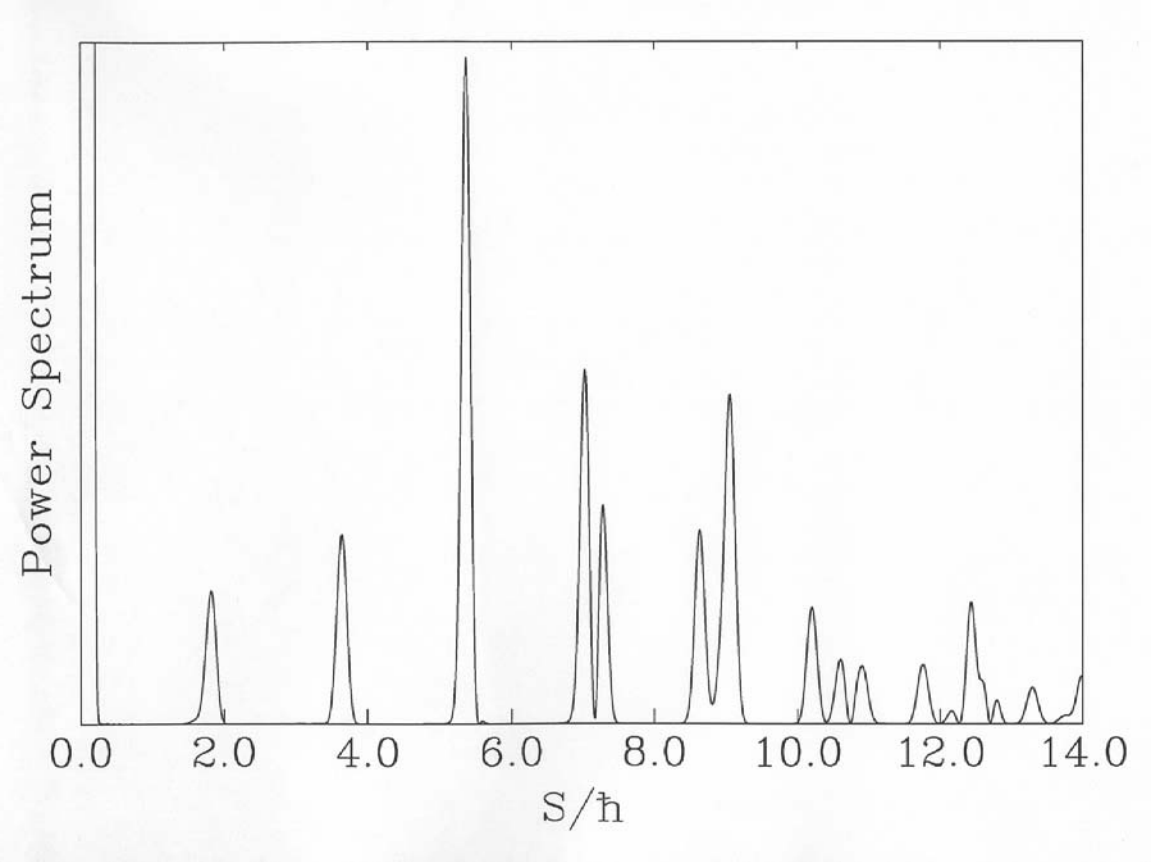

Figure 3: The power spectrum of the density of states of Figure 2.