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Effects of surface roughness on the electronic structure of metallic clusters

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Abstract. We study the electronic level density in spherical clusters. Due to the granularity of the ionic background the surface is irregular at the microscopical level. We show that this affects the shell structure and that the level statistics display from the bottom to the top of the spectrum a transition from a poissonian behaviour to one consistent with the predictions of random matrices theory.

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1. Introduction

The interest in the study of quantum finite size effects in small metallic aggregates and clusters has been stimulated in the last few years through the availability of molecular beams and the discovery of electronic shell structure in simple metal clusters [1]. The quantization of electronic orbits was initially studied for very small clusters, and was also recently observed for large numbers of electrons [2, 3]. One now reaches from below a regime that could be called the "intermediate size regime" and which is reached from above in the physics of minute metallic particles. In this regime electronic quantum effects still play an important role, but the exact solution of the full quantum mechanical problem is not necessary for the description of the measurable properties of the cluster. This leads to a type of "statistical approach" which we will present below. It is justified by the complexity of the problem and by the large number of configurations available in a molecular beam for a cluster of a given size.

This type of study was initiated by Kubo [4] who calculated in particular the specific heat and spin susceptibility of metallic aggregates at low temperature assuming a random uncorrelated sequence of electronic levels (a "poissonian" spectrum). This approach was then extended by Gor'kov and Eliashberg [5] who emphasized the importance of correlations in the – still random – spectrum, linked to basic symmetries of the Hamiltonian through the theory of random matrices (RMT, for a review see [6]). The importance of the level statistics on specific heat, dielectric and magnetic susceptibility and odd-even effects for these observables was pointed out (see for instance [7]). More recently it was also found to be determining for the odd-even abundance rate in molecular beams of alkali clusters [8].

In [9] the level spacings distribution of small metallic particles with random impurities was shown to follow the prediction of RMT. In the present paper we will study the effects of surface roughness on clusters with a fixed spherical shape (throughout this paper we use the concept of roughness in a loose sense which implies only that the clusters have small size surface irregularities). This is so to say the minimal – and unavoidable – type of disorder that a cluster can have; it is only caused by the discrete nature of the ionic background seen by the valence electrons. In this case the problem of determining the type of level statistics has not received a definite theoretical answer. The purpose of this paper is to try to clarify the domain of applicability of RMT and to study a possible transition from a poissonian spectrum to one of those predicted by RMT. We will be here interested in alkali clusters where the spin-orbit coupling is negligeable and the relevant ensemble of random Hamiltonians would be the gaussian orthogonal ensemble, GOE (cf. [6]).

The paper is organized as follows. In Sect. 2 we develop for a single cluster a simple model containing the essential physical picture. In Sect. 3 we simulate an ensemble of rough clusters and analyse the fluctuations of the spectrum and the wave functions. Finally we compare our results with previous works and present our conclusions in Sect. 4.

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2. The model

Surface roughness will be most easily described within the tight-binding method as was done in [10, 11]. Since the valence electrons of the alkali metals we are interested in form an almost free electron gas, we must construct a tight-binding model where the effects of the underlying lattice are as weak as possible. The route we have chosen is to consider a model with only one valence s-electron per atom and to allow for hopping and overlapping of the atomic orbitals up to the third neighbour. More precisely, if we label the ionic sites by the set of points $\{\mathbf{R}\}$ and an atomic orbital located around point $\mathbf{R}$ by $|\mathbf{R}\rangle$, we will have the following matrix elements for the Hamiltonian:

$$\langle \mathbf{R}|H|\mathbf{R}'\rangle = \begin{cases} \alpha & \text{if } \mathbf{R}'=\mathbf{R}, \\ \beta_1 & \text{if } \mathbf{R}'=\mathbf{R}+\Delta_1, \\ \beta_2 & \text{if } \mathbf{R}'=\mathbf{R}+\Delta_2, \\ \beta_3 & \text{if } \mathbf{R}'=\mathbf{R}+\Delta_3, \end{cases} \tag{1}$$

and $\langle \mathbf{R}|H|\mathbf{R}'\rangle = 0$ otherwise.

In (1) Δ_1 (resp. Δ_2 and Δ_3) is a generic name for the vector separating two nearest (resp. second and third) neighbours. We will in the following choose the zero of energies such that $\alpha=0$ and the units such that $\beta_1=-1$. For the overlapping of the wave functions we take:

$$\langle \mathbf{R}|\mathbf{R}'\rangle = \begin{cases} 1 & \text{if } \mathbf{R}'=\mathbf{R}, \\ \mathscr{S}_1 & \text{if } \mathbf{R}'=\mathbf{R}+\Delta_1, \\ \mathscr{S}_2 & \text{if } \mathbf{R}'=\mathbf{R}+\Delta_2, \\ \mathscr{S}_3 & \text{if } \mathbf{R}'=\mathbf{R}+\Delta_3, \end{cases} \tag{2}$$

and $\langle \mathbf{R}|\mathbf{R}'\rangle = 0$ otherwise.

The matrix elements of the Hamiltonian decrease with the distance between $\mathbf{R}$ and $\mathbf{R}'$ roughly with the same rate as the overlapping of the wave functions. We thus take for simplicity:

$$\frac{\mathscr{S}_1}{\beta_1}=\frac{\mathscr{S}_2}{\beta_2}=\frac{\mathscr{S}_3}{\beta_3}\equiv -\mathscr{S}. \tag{3}$$

Since we are only interested in surface irregularities we will consider that the bulk structure of the cluster is ordered and we will put the background ions on a lattice. We will present here the results for a bcc lattice. We have checked that the fcc structure leads to the same qualitative effects.

As an asymptotic limit of the model we now study the band structure obtained with the Hamiltonian (1) and the atomic orbitals (2), keeping in mind that we want to imitate the main features of almost free electrons in a crystalline solid. The most important effect of the free electrons model is the spherical and isotropic Fermi surface. For the tight-binding model on the contrary, the breaking of the continuous translational symmetry by the lattice is quite noticeable due to the importance of the scattering centers. This leads for the band structure to a dispersion relation which is not quadratic but which has the following form (see e.g. [12]):

$$E(\mathbf{k}) = \frac{\sum_{n=1}^{3} \sum_{\Delta_n} \beta_n \exp(i\mathbf{k}\cdot\Delta_n)}{1+\sum_{n=1}^{3} \sum_{\Delta_n} \mathscr{S}_n \exp(i\mathbf{k}\cdot\Delta_n)}, \tag{4}$$

where $\mathbf{k}$ is the wave vector. The low-k expansion of (4) will always start with a quadratic behaviour. This is to be linked to the result of [13] where a simple tight-binding model was shown to be equivalent to a free electron model in the long wave length limit. We shall seek the low-k expansion to be as quadratic and isotropic as possible. With our 3 free parameters (β_2, β_3 and $\mathscr{S}$) we can impose an expansion of the form:

$$E(\mathbf{k}) = E_0 + E_2(ak)^2 + E_6(ak)^6 + \mathcal{O}(a^8k^8), \tag{5}$$

where a is the lattice constant. We impose in (5) that the term in $(ak)^4$ is zero to remain as close to the free electron model as possible. Besides we have at order k^6 a term which is sill isotropic i.e. proportional to $k^6 = |\mathbf{k}|^6$. The requirements of (5) are fulfilled by the choice

$$\beta_2 = -\tfrac{5}{8}, \quad \beta_3 = -\tfrac{1}{16}, \quad \text{and} \quad \mathscr{S} = \tfrac{1}{25} \tag{6}$$

leading then to values $E_0 = -25/3$, $E_2 = 5/6$ and $E_6 = -1/1080$. The resulting band structure of (4) is shown in Fig. 1. One sees that the dispersion relation is not very different from the one of a free electron, and more interesting, the anisotropy in the ΓN, ΓP and ΓH directions in reciprocal space is small. This can be more clearly seen on Fig. 2 where we represent two cuts of the first Brillouin zone and of the Fermi surface. The improvement compared with the simpler "Hückel model" ($\mathscr{S}=0$, $\beta_2=\beta_3=0$) is very significant. If we denote by k_0 the Fermi momentum of free electrons in the bcc

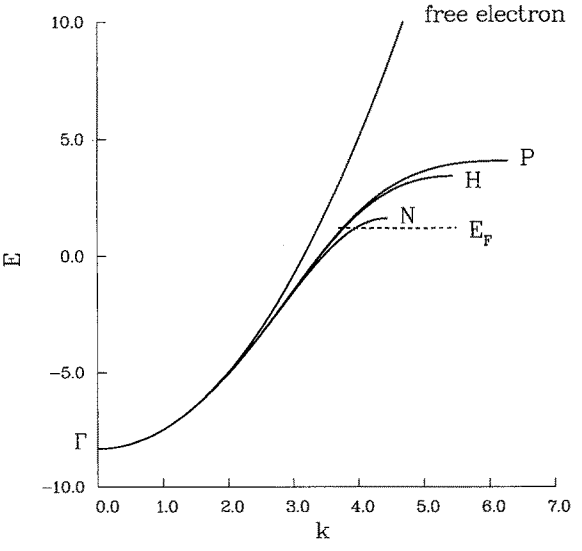

Fig. 1. Dispersion relations (4) along the axes ΓN, ΓP and ΓH of reciprocal space. The *upper curve* is the free electron result. The *horizontal dashed line* indicates the Fermi energy of our model which we determined numerically to be $E_F \simeq 1.18$. The location of points Γ, N, P and H in the first Brillouin zone is shown on Fig. 2. The unit of momentum is $1/a$

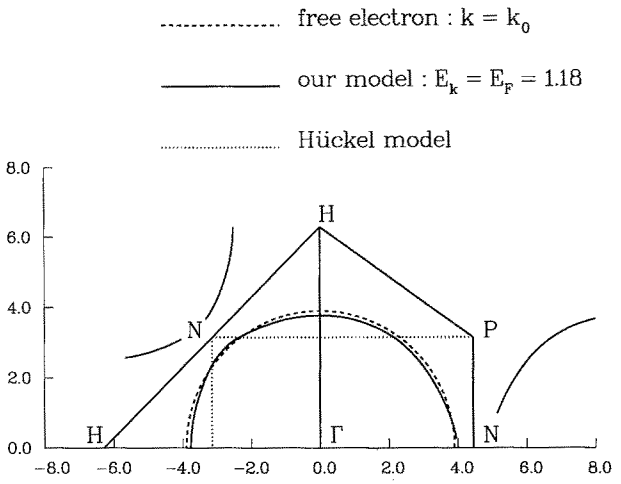

Fig. 2. Cross sections of the Fermi surface (*solid line*) and of the first Brillouin zone (*straight solid lines*). The Fermi energy was numerically estimated to be $E_F \simeq 1.18$. The *dashed line* is the free electron result $k_0 = (6\pi^2)^{1/3}/a$. The *dotted line* is the result of the simplest tight-binding model: the Hückel model (defined by $\mathscr{S}=0$, $\beta_2=\beta_3=0$). The unit of momentum is $1/a$

lattice ($k_0=(6\pi^2)^{1/3}/a$) the fluctuations $\Delta k/k_0$ on the Fermi surface of our model are of about 5%. This is comparable with the fluctuations for Cs($\simeq 3.3\%$) but much larger than for Na($\simeq 0.1\%$) (see [12]). Nevertheless, up to an energy $E=-1$ the anisotropy in our model is negligeable (see Fig. 1) and we will devote the main part of our study to this region of the clusters' spectra. The breaking of the large shell effects that an electron would experience in a perfectly spherical cluster will then be only caused by the surface irregularities since we have minimized the effects of the symmetry of the underlying lattice.

3. Rough spherical clusters

We now turn to the simulation of an ensemble of rough spherical clusters. Starting from a point **C** in real space we construct a spherical cluster by eliminating all the lattice points which are at a distance from **C** greater or equal than a fixed value r_0. In our example we chose $r_0 = 3a\sqrt{2}$, i.e. 3 times the distance to the third neighbour on the bcc structure. In order to avoid degeneracies related to the $\mathcal{O}_h$ symmetry of the underlying lattice we take care that the center **C** is not a lattice point or a point of symmetry. Varying the position of **C** we then generate a set of 50 different clusters. These clusters are spherical on the coarse grained level but they have each a different rough microscopic structure. They do not contain exactly the same number of atoms: in our simulations it varies from 626 to 648 atoms; however this small variation ($\pm 2\%$) does not affect the statistical features of the spectrum and of the wave functions. Moreover, studying spectra coming from clusters with different sizes (and shapes) makes sure that we do not analyse redundant information and that our 50 sets of data are indeed independent.

In Fig. 3 we present the spectrum of one of the clusters and compare it with the spectrum of the system composed by one particle in a spherical cavity with infinite walls (the mass of this particle and the energy inside the cavity are chosen to match (5) up to k^2, we refer to this system as the "equivalent sphere"). In order to compare the spectra easily we have plotted the integrated level densities:

$$N(E) = 2\sum_i \theta(E - E_i). \tag{7}$$

The factor 2 accounts for spin degeneracy, θ is the Heaviside function and the E_i's are the eigenvalues. All the essential degeneracies of the sphere are broken in the cluster case (although it is sometimes not noticeable on the figure), but the large scale features of the spectra are very similar. Therefore in order to analyse our data and determine the level statistics we must study the spectrum *shell by shell*, otherwise we might mix two effects: one linked to the large scale poissonian statistics of the sphere and the other being the perturbation of the levels resulting from the surface roughness [14]. If one goes up in energy, the electronic wave length becomes comparable with the typical size of the surface bumps (i.e. the lattice constant a): the breaking of the degeneracies becomes more and more important and shells begin to overlap. Around the Fermi energy, the wave length is $\sim a$ and the spherical shell structure is washed out (see the insert in Fig. 3). So our model – or any type of Hückel approximation – would not predict reliable magic numbers, because it misses the shell structure near E_F, where it is the most important for determining the total energy.

We analyzed the level statistics for the following energy intervals: $40 < N(E) \leqq 58$, $68 < N(E) \leqq 92$ (resulting from the overlap of the shells 1 h and 3 s, see Fig. 3), $138 < N(E) \leqq 186$ (shells $1j$ and $2g$) and $1.0 \leqq E \leqq 1.4$, i.e. around the Fermi energy $E_F \simeq 1.18$ (the distinction between different shells is here no longer necessary).

Let us make a technical remark: In order to compare the spectra coming from different clusters we "unfold" each spectrum in the interval of interest (see e.g. [15]); i.e. we fit locally the level density $N(E)$ by a smooth function $N_{av}(E)$ and define new dimensionless levels $\varepsilon_i = N_{av}(E_i)$. Thus in all the intervals the new spectra have the same average density equal to unity and it is then legitimate to add the fluctuations coming from different spectra. The function N_{av} was chosen to be a straight line for the 3 first intervals and a parabola around the Fermi energy.

A usual observable in the analysis of spectra is the level spacings distribution $P(\Delta)$ giving the probability that 2 successive levels ε_i and ε_{i+1} are separated by an energy Δ. It is plotted on Fig. 4 where we see clearly when going up in energy a transition from a poissonian distribution to the Wigner surmise [6, 15] characteristic of GOE. The same transition is seen on the spectral rigidity [6, 15] $\Delta_3(L)$ (cf. Fig. 5). $\Delta_3(L)$ is the last-square deviation of the integrated level density $N(\varepsilon_i)$ from a straight line fitting it on an interval of length L. It mea-

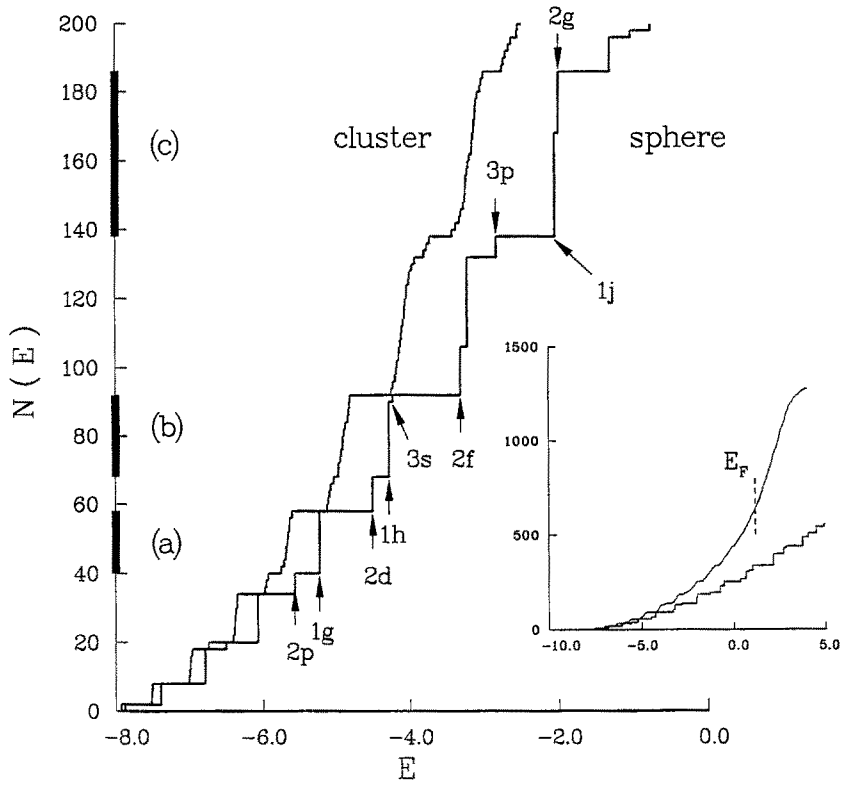

Fig. 3. Cumulated level density of the lower part of the spectrum of a typical cluster and of the equivalent sphere (see the text). The *thick lines* on the vertical axis are located on the intervals (a), (b) and (c) analyzed in the following. The *arrows* indicate some of the spherical shells important for the analysis. The insert displays the complete figure. For the cluster considered the Fermi energy is 1.17 and appears as a *dashed vertical line* in the insert

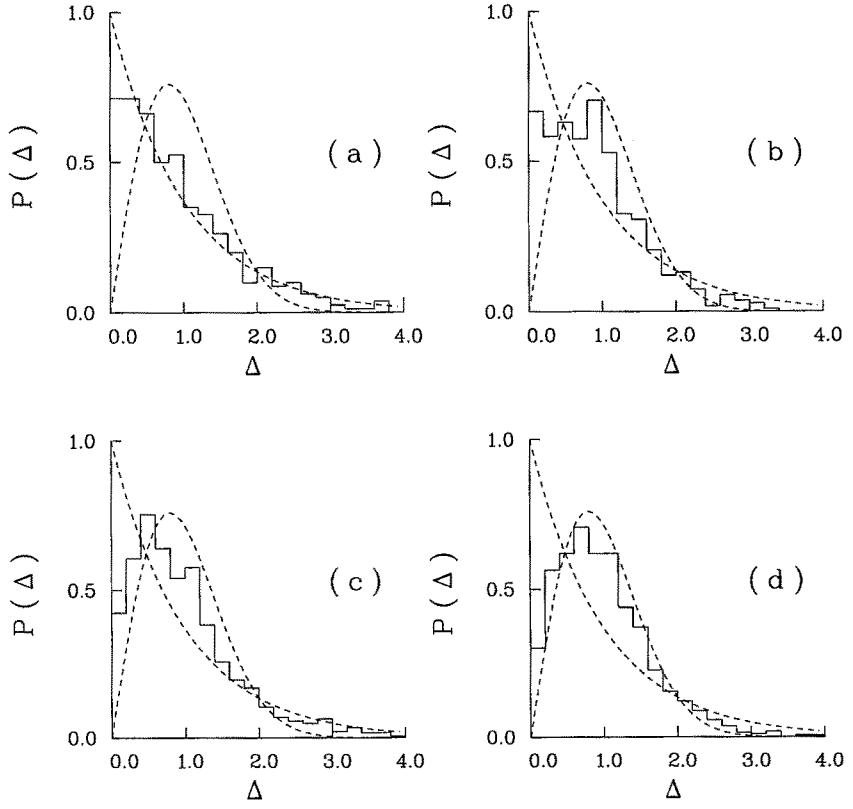

Fig. 4. Level spacings distribution. case (a): $40 < N(E) \leqq 58$ (with 400 spacings included), case (b): $68 < N(E) \leqq 92$ (541 spacings included), case (c): $138 < N(E) \leqq 186$ (1149 spacings), case (d): $1.0 < E \leqq 1.4$ (1881 spacings). The *dashed lines* represent the poissonian result $P(\Delta) = \exp(-\Delta)$ and the Wigner surmise for GOE: $P(\Delta) = \pi\Delta/2 \times \exp(-\pi\Delta^2/4)$

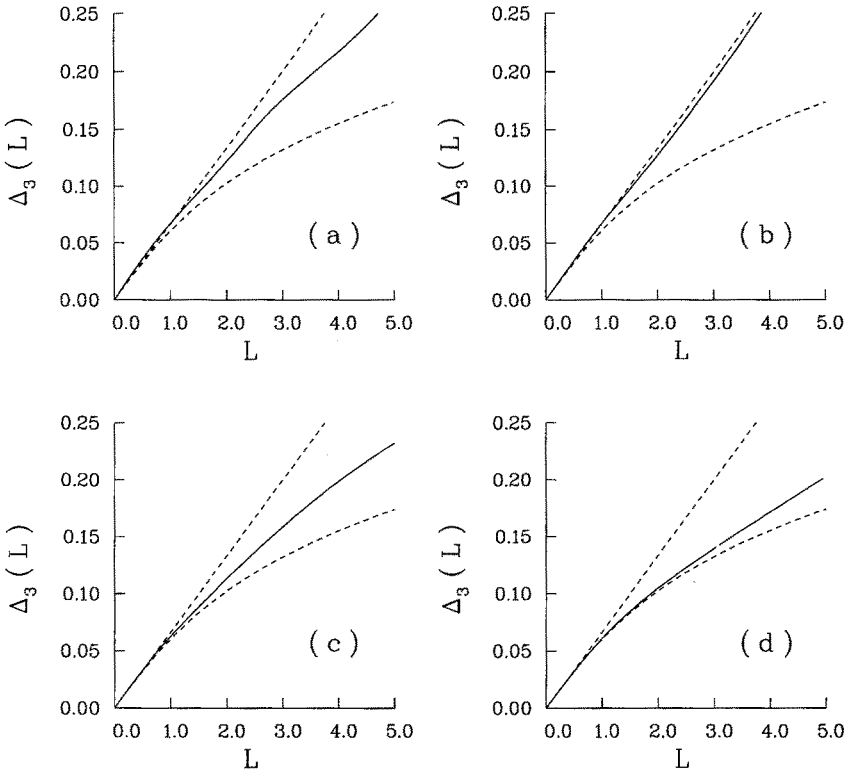

Fig. 5. Spectral rigidity. The label a, b, c, d refer to the same cases as in Fig. 4. The *upper dashed line* represents the poissonian result ($\Delta_3(L)=L/15$) and the *lower dashed line* is the GOE prediction

sures the fluctuations of the spectrum on a scale L: the smaller is Δ_3, the stronger is the rigidity i.e. the correlations in the spectrum. One sees on Fig. 5 as one goes up in energy that the rigidity increases*, i.e. the correlations of eigenvalues due to the surface roughness increase.

In view of these results we are lead to assume that the problem can be put in the form of the perturbation of a Hamiltonian having a spherical symmetry. The effects of this perturbation increase with the energy: in the bottom of the spectrum the de Broglie wave-length is large in comparison with the surface irregularities and the perturbation is accordingly small. In this region of the spectrum we got a poissonian distribution of the eigen-energies. When going up in the spectrum, the perturbation becomes more and more important and our results indicate a transition towards statistical feactures consistent with the predictions of RMT.

In order to give further support to this qualitative picture we will now define a basis of "unperturbed states" and study the coordinates of the eigen-functions in this basis. The simplest way to define these unperturbed states is to take the solution of Schrödinger equation in a sphere with infinite hard walls. In our model the wave functions are essentially of discrete nature, or more precisely they are characterized only by their components on the set of atomic orbitals. In accordance with this feature we define a discrete version of the "unperturbed basis":

$$|nlm\rangle = A_{nlm} \sum_{\mathbf{R}} j_l(z_{nl}\, R/r_0)\, Y_{lm}(\hat{R})\, |\mathbf{R}\rangle, \tag{8}$$

where A_{nlm} is a normalization coefficient, r_0 is the radius of the sphere, Y_{lm} is a spherical harmonic, and z_{nl} is the n^{th} zero of the spherical Bessel function of the first kind j_l. For the first twenty unperturbed shells we have checked numerically that the $|nlm\rangle$'s where orthogonal to a very good accuracy ($\lesssim 5\cdot 10^{-3}$).

Since we have now an appropriate orthonormalized basis we can study the influence of surface roughness on these "unperturbed" wave functions. For a given cluster and a given electronic eigenstate $|\Psi_i\rangle$ (solution of $H|\Psi_i = E_i|\Psi_i\rangle$) we study the components $|\langle nlm|\Psi_i\rangle|^2$. They can vary for different choices of the unperturbed basis because the m index is not here an essential quantum number but serves merely for labelling the wave-functions. Nevertheless the quantity

$$S_{nl}(\Psi_i) = \sum_m |\langle nlm|\Psi_i\rangle|^2 \tag{9}$$

represents the square of the norm of the projection of the state $|\Psi_i\rangle$ on the (nl) subspace and does not depend on the choice of the unperturbed basis. If the roughness does not affect the system to much, then a state $|\Psi_i\rangle$ will belong to a given (nl) shell and $S_{nl}(\Psi_i)$ will be 1 on this particular shell and 0 elsewhere. This is indeed what is observed in Fig. 6 for states at the bottom of the spectrum. When energy increases the roughness mixes the shells and the "strength" $S_{nl}(\Psi_i)$ gets more spread. For instance, one sees clearly on the histograms of Fig. 6 that the shells $1j$ and $2g$ are mixed, as was

* There is however a departure from the poissonian prediction in case (a) of Fig. 5. We believe it is due to the lack of statistics. Nevertheless the general trend is very clear

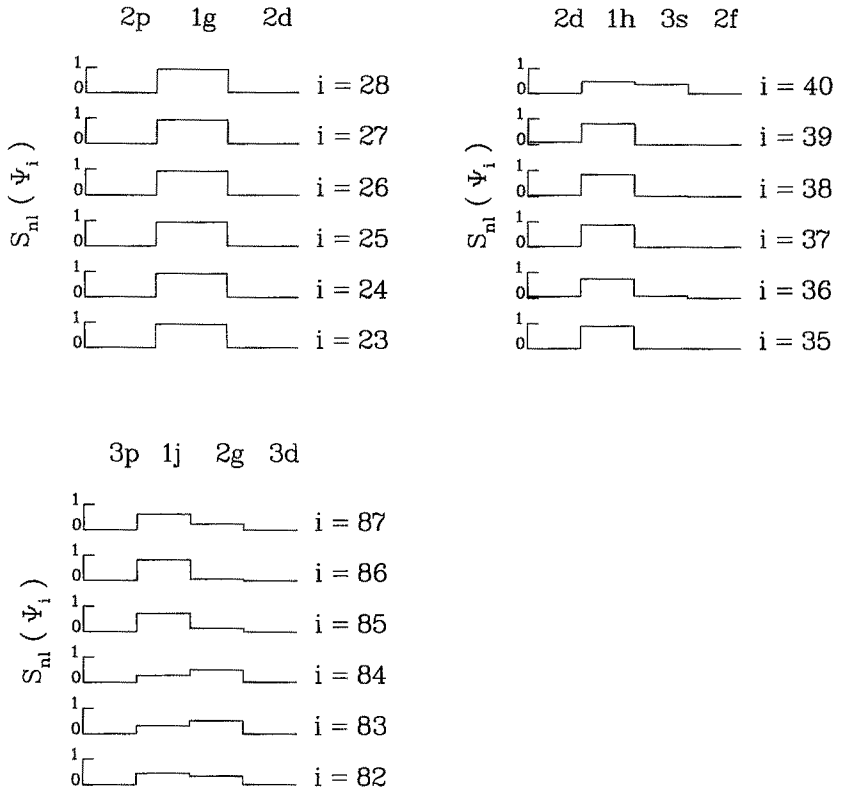

Fig. 6. Strength functions $S_{nl}(\Psi_i)$. The number i of each state appears at the right of its strength. The shells (nl) on the abscissa axis are ordered like the shells of the equivalent sphere: $1s$, $1p$, $1d$, $2s$ ... The total amount of strength displayed is of about 93% for $23 \leqq i \leqq 28$ and goes to $\sim 85\%$ for $82 \leqq i \leqq 87$

anticipated from Fig. 3. For each state $|\Psi_i\rangle$, this spreading of the strength on several shells can be characterized by a participation ratio κ_i [16] defined by:

$$1/\kappa_i = \sum_{nl} |S_{nl}(\Psi_i)|^2. \tag{10}$$

κ_i is 1 if the state remains inside a single shell, and is equal to N if the strength of $|\Psi_i\rangle$ is equally shared by N unperturbed shells. Thus κ_i can be viewed as an effective number of shells on which the strength of state $|\Psi_i\rangle$ would be concentrated. For the cluster from which we have plotted the strength in Fig. 6 we found in the interval (a) a mean value of the participation ratio $\bar{\kappa} = 1.17$, for the interval (b) $\bar{\kappa} = 1.53$ and for case (c) $\bar{\kappa} = 2.49$.

This enhances our previous picture: both the results for the eigen-energies and the eigen-functions of our tight-binding model appear as perturbations of a Hamiltonian with spherical symmetry. As stated above the effects of the perturbation increase with the energy, leading to shell-mixing and to level statistics reaching the results of RMT.

4. Conclusion

The three tools we have used for our analysis (short range correlations in the spectrum with $P(\Delta)$, longer range modulations through $\Delta_3(L)$ and a study of the wave functions) lead to the following qualitative picture: in the lower part of the spectrum the de Broglie wavelength being large, surface irregularities do not perturb the eigenstates much and there is a strong bunching of levels. This shell effect disappears gradually for increasing energies. Moreover, the perturbation causes a mixing of levels *inside a shell* which is poissonian at the bottom of the spectrum and becomes gradually gaussian (GOE). However, for the perturbation we have considered here, even at the Fermi energy the statistical features of the spectrum are not in complete agreement with the results of RMT. This indicates that for weak disorder and equivalently for low band filling – i.e. when the Fermi energy is in a region of the spectrum where the perturbation is small – the approach of RMT ceases to be valid.

These features of the spectrum including the Poisson to GOE transition were in substance present in earlier studies. In [11], Bucher et al. used a Hückel model to describe clusters more rough than ours. In the bottom of their spectra they observed a shell effect that disappears for increasing surface roughness (cf. Fig. 6 of [11]). They obtain a level spacing distribution near the Fermi energy which is GOE-like and at the bottom of the spectrum it would certainly be poissonian if corrected for the shell effect (see their Fig. 5a). In [17] Ratcliff maps a model of free electrons in an irregular sharp surface onto a system enclosed in a sharp sphere with a potential treated perturbatively. The system has the same symmetry as ours, and indeed the level spacing distribution is in agreement with the Wigner surmise for the particular shell considered in [17]. The surface irregularities are expanded as a linear combination of spherical harmonics $Y_{\lambda\mu}$. Our study would correspond to high λ deformations (small bumps at the surface), the matrix elements of this deformation inside a given shell l decrease and become zero for $l < \lambda/2$. We thus expect that the same

transition would be seen in the model of [17], and similarly in a jellium model. However, in this type of models the shell structure at the Fermi energy is larger than in a tight-binding approximation, and the effects of surface roughness near E_F are then expected to be weakened compared to our case.

The level spacing of disordered metallic particles was shown by Efetov [9] to follow the RMT predictions. This result is derived in the case of random impurity potentials distributed with a gaussian correlation function and in the limit where the perturbation induces a shift of the levels large compared with the mean level spacing. This last condition is certainly not fulfilled at the bottom of our spectra; but when the shells begin to overlap we reach the range of validity of Efetov's approach and we get similar results (although the physical origin of the disorder is not the same). In addition our numerical study indicates that the RMT approach fails in the bottom of the spectrum and that the Poisson statistics is then appropriate.

Finally let us note that in our model we have put the ionic cores on a lattice and implicitly assumed that the clusters are solid-like. We know that this is true for large enough sizes below a certain temperature but in other cases we expect the clusters to have an amorphous structure or a non crystalline order (see e.g. [18]). It would then be of interest to study the electronic properties of these structures in connection with the experimental result of [2] where the packing of the ionic cores in closed icosahedral structures was seen to correlate with an important increase of the ionization potential of the cluster.

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