TWO EXAMPLES OF ELECTRONIC SPECTRUM FLUCTUATIONS IN MICROPARTICLES ☆

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We analyse the nearest-neighbour spacing distribution of the electronic spectrum of microparticles in two cases: a truncated octahedron consisting of 38 Ni atoms and a Ti catalytic complex formed by 24 atoms. In both cases a Poisson distribution is obtained.

The low-temperature thermodynamic and electromagnetic properties of electrons in small aggregates of atoms (such as microclusters or small metallic particles) depend on the spacing distribution of the electronic levels in the neighbourhood of the Fermi level [1]. It has been argued [2,3], without formal justification, that irregularities in the small particle surface will affect the level-spacing distribution. Kubo [2] assumed that a completely random sequence of levels would be obtained and, therefore, that the spectrum fluctuations would be of the Poisson type. On the other hand, Gor'kov and Eliashberg [3] assumed that surface irregularities, being of the order of atomic size, would induce random interactions of the electrons with the walls. These authors stated that this situation is analogous to that encountered in determining the distribution of high-excitation levels in nuclei, for which random-matrix theory is applicable [4]. If this last assumption is valid, the phenomena of level repulsion (i.e. the absence of small spacings in the distribution) will appear. It should be remarked that both approaches [2,3] were given the same qualitative justification, so a closer analysis is required to establish which spacing distribution is more appropriate for electron energy levels in small aggregates of atoms.

Assuming that the free-electron model is as good to describe electrons in small particles as it is for the metal in bulk, two recent works [5,6] have analysed in more detail the influence of surface irregularities on the electronic spectrum fluctuations. In the first paper [5] it is shown that the problem of Dirichlet boundary conditions cannot be formulated in a straightforward way in terms of matrices. Furthermore, a Poisson spacing distribution was obtained for an assembly of rectangular bidimensional particles. This indicates that random matrix ensembles might not be appropriate to describe the electronic spectrum fluctuations in small particles. More recently [6], the influence of surface irregularities has been dealt with, using a perturbative approach, by defining an effective hamiltonian which has, in the unperturbed region bounded by a smooth surface, the same eigenvalues as the free-electron hamiltonian has in the region bounded by an irregular surface. In the particular example in which the smooth surface is a sphere and the perturbed boundary is very irregular, Tavel et al. obtain a spacing distribution of the Wigner type, which shows level repulsion [4]. We therefore see that the two above mentioned works reach to different conclusions.

In this paper we shall provide more evidence re-

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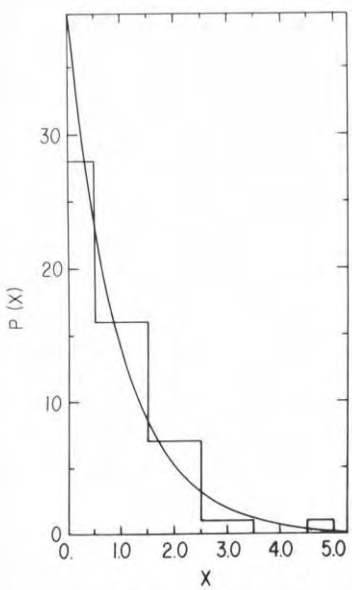

Fig. 1. The distribution $P(x)$ of nearest-neighbour level spacings x corresponding to the Ni-cluster d-band [7], the degeneracy of the 78 levels considered in the histogramme was not taken into account. The histogramme fits very well with the Poisson distribution e^{-x}, the probability of χ^2 being 89%.

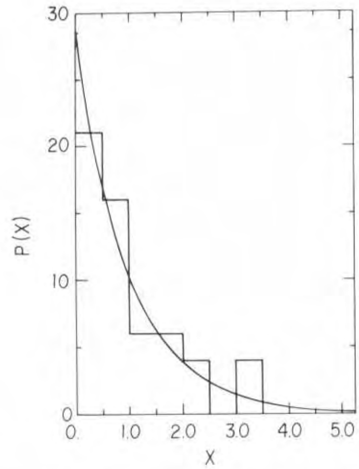

Fig. 2. Nearest-neighbour spacing distribution $P(x)$ corresponding to the electron orbital energies of the Ti-catalytic complex [8]. The histogramme is constructed by taking into account 58 energy levels between −1.2 and 0.6 au around the Fermi level. The fit to the Poisson distribution is very good, the probability of χ^2 being 93%.

garding the spacing distribution of electronic levels in small aggregates of atoms. In distinction to what has been done before, we shall here depart from the free-electron picture, making use of "realistic" calculations in which the electron–electron and the electron–nucleus Coulomb interaction are taken into account. In other words, instead of defining the particle boundary, the atoms are given a fixed geometry for which the electron energy levels are computed. We now present the results for two different examples. The first example refers to the electronic structure of a 38-Ni cluster whose geometrical configuration is a face-centered truncated octahedron, with six square (100) and eight hexagonal (111) faces, all edges being of equal length. The energies of d-electrons were obtained within the tight-binding approximation by Cyrot-Lackmann et al. [7]. The nearest-neighbour spacing distribution is given in fig. 1, which shows that a Poisson distribution applies for this case. The second example is provided by the orbital electron energies computed for the complex $TiCl_4 \cdot Al(CH_3)_2 \cdot C_2H_7$ (catalyst + C_2H_4) in the context of a Ziegler–Natta type reaction. For this system an *ab-initio* all-electron LCAO-SCF calculation was reported recently [8]. The nearest-neighbour spacing distribution, considering 58 levels around the Fermi level, is shown in fig. 2, where it can be seen that it is again of the Poisson type. Both histogrammes were obtained after eliminating level density variations through an unfolding procedure [9].

From these two examples, in which the free-electron model was not assumed, we again obtain some indication that the Poisson spacing distribution might be more adequate to represent the electronic spectrum fluctuations in very small aggregates of atoms. It should be pointed out that a definite answer to this problem has certainly not been obtained from the theoretical point of view. A review [10] of the observed low-temperature properties of small particles also shows that the experimental situation is not at all clear. A definite answer will only come from the comparison of theoretical [11,12] and experimental results, which are now beginning to accumulate [1].

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References

[1] Proc. Intern. Meeting on Small particles and inorganic clusters (Lyon, France, 1976); J. Physique 38 (1977) C2-129.
[2] R. Kubo, J. Phys. Soc. Japan 17 (1962) 975.
[3] L.P. Gor'kov and G.M. Eliashberg, Sov. Phys. JETP 21 (1965) 940.
[4] C.E. Porter, ed., Statistical theories of spectra (Academic Press, New York, 1965);
M.L. Mehta, Random matrices (Academic Press, New York, 1967).
[5] J. Barojas, E. Cota, E. Blaisten-Barojas, J. Flores and P.A. Mello, Ann. Phys. 107 (1977) 95.
[6] J. Tavel, Ph.D. thesis, State Univ. of New York at Albany USA (1978);
J. Tavel, K. Ratcliff and N. Rosenzweig, to be published;
J. Tavel, K. Ratcliff and M. Tavel, to be published.
[7] F. Cyrot-Lackmann, M.C. Desjonquères and M.B. Gordon, J. Physique 38 (1977) C2-57.
[8] O. Novaro, E. Blaisten-Barojas, E. Clementi, G. Giunchi and M. Ruiz-Vizcaya, J. Chem. Phys. 68 (1978) 2337.
[9] S.S.M. Wong and J.B. French, Nucl. Phys. A198 (1972) 188.
[10] T.A. Brody, J. Flores, P.A. Mello, J.B. French and S.S.M. Wong, Random matrix physics: spectrum and strength fluctuations, Ch. 9, to be published.
[11] R. Denton, B. Mühlschlegel and D.J. Scalapino, Phys. Rev. B7 (1973) 3589.
[12] E. Blaisten-Barojas, J. Flores, P.A. Mello, J. Barojas and E. Cota, Phys. Lett. 61A (1977) 146.