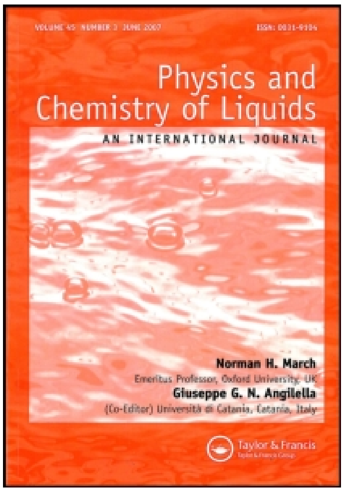

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WKB LEVEL SPECTRA IN TWO INHOMOGENEOUS ELECTRON LIQUIDS: Na CLUSTERS AND C CAGES

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After a brief summary of known magic numbers and eigenvalue sums for (a) the hydrogenic potential $-Ze^2/r$ and (b) the three-dimensional isotropic harmonic oscillator potential, approximate semi-classical scaling laws are presented relating to WKB eigenvalues for two more complex central potentials $V(r)$. The first is the so-called Woods-Saxon potential, used in early work to calculate electronic magic numbers in clusters of Na atoms. The second potential $V(r)$ chosen arises from a simple surface charge model of almost-spherical carbon cages such as C_{60}. For these last two potentials, semi-classical theory is shown to lead to qualitative insight, without very lengthy mathematical calculations.

Keywords: Inhomogeneous electron liquids; Magic numbers; Eigenvalue sum scaling

I. INTRODUCTION

Quantum mechanical courses often start with the bound states of a potential well, followed sometimes by a discussion of magic numbers in nuclei and in the Periodic Table of elements, based on harmonic confinement and on a hydrogenic spectrum, respectively. Of course, to obtain the correct magic numbers for nuclei requires a more advanced treatment involving spin-orbit coupling.

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Here too, we shall begin with the three-dimensional isotropic harmonic oscillator with its eigenvalue spectrum $\varepsilon_{n_x,n_y,n_z}$:

$$\varepsilon_{n_x,n_y,n_z} = (n_x + n_y + n_z + 3/2)h\nu \tag{1.1}$$

where ν is the classical frequency of the oscillator. The levels, in fact, can be labelled with a total quantum number N given by

$$N = (n_x + n_y + n_z), \tag{1.2}$$

the degeneracy g_N of $\varepsilon_{n_x,n_y,n_z} \equiv \varepsilon_N$ being given by the number of ways a given N can be made up of positive integers n_x, n_y and n_z, including zero, *via* Eq. (1.2).

With fermions doubly filling the oscillator levels (1.1), the magic numbers N_m are 2 ($n_x = n_y = n_z = 0$), 8 (2 + the three doubly-filled levels corresponding to $n_x, n_y, n_z = 1, 0, 0$ and permutations), 20, *etc.*, where, for the $\mathcal{N}th$ closed shell

$$N_{\mathcal{N}} = \frac{1}{3}(\mathcal{N}^3 + 3\mathcal{N}^2 + 2\mathcal{N}), \tag{1.3}$$

which is readily verified to reproduce the three magic numbers cited above. We now turn to the eigenvalue sum $E_s^{(N)}$ corresponding to these magic numbers $N_{\mathcal{N}}$. For the first closed shell $\mathcal{N} = 1$, corresponding to $N = 0$ in Eqs. (1.1) and (1.2), $\varepsilon_1 = (3/2)h\nu$, and with double degeneracy

$$\frac{E_s^{(1)}}{h\nu} = 3 \equiv e_s^{(1)}$$

in dimensionless form. Evidently

$$e_s^{(2)} = 3 + 6 \cdot \frac{5}{2} = 18$$

and

$$e_s^{(3)} = 3 + 15 + 12 \cdot \frac{7}{2} = 60$$

etc. In general we can write

$$e_s^{(\mathcal{N})} = \sum_{N=0}^{\mathcal{N}-1} 2g_N\left(N + \frac{3}{2}\right)$$

with $g_N = ((N+1)(N+2))/2$ the level degeneracy for the total energy $(N+3/2)h\nu$. Then, summing [1], we have

$$e_s^{(\mathcal{N})} = \frac{\mathcal{N}}{4}[\mathcal{N}^3 + 4\mathcal{N}^2 + 5\mathcal{N} + 2]$$

It is worthy of note that Shea and Aravind [2] have discussed the degeneracy for the harmonic oscillator (also for the square well and for the hydrogen atom) in arbitrary dimensions. Such considerations are currently of interest in relation to Fermion vapours.

Turning to the simpler H-like atom case in this context,

$$\varepsilon_n = -\frac{Z^2e^2}{2n^2a_o}, \quad a_o = \frac{\hbar^2}{me^2}$$

and a closed shell of principal quantum number n contains $2n^2$ electrons with paired spins, so that with $\mathcal{N}$ closed shells

$$\frac{E_s^{(\mathcal{N})}}{(Z^2e^2/a_o)} = e^{(\mathcal{N})} = -\mathcal{N} \tag{1.4}$$

while the magic numbers $N_{\mathcal{N}}$ are given by [1]

$$N_{\mathcal{N}} = \sum_1^{\mathcal{N}} 2n^2 = \frac{\mathcal{N}(\mathcal{N}+1)(2\mathcal{N}+1)}{3} = \frac{1}{3}(2\mathcal{N}^3 + 3\mathcal{N}^2 + \mathcal{N}). \tag{1.5}$$

Evidently, by solving the cubic equation (1.5) for $\mathcal{N} = \mathcal{N}(N_n)$ it follows from Eq. (1.4) that

$$e^{(\mathcal{N})} = e(N_n). \tag{1.6}$$

For $\mathcal{N}$ sufficiently large, Eq. (1.5) yields

$$\mathcal{N} \simeq \left(\frac{3}{2}\right)^{1/3} N_n^{1/3}$$

and hence

$$e(N_n)|_{N_n\to\infty} \simeq -\left(\frac{3}{2}\right)^{1/3} N_n^{1/3} \tag{1.7}$$

If we insist on the 'neutrality' condition $N_n = Z$, then we find

$$E_{sum}^{N_n=Z} = -\left(\frac{3}{2}\right)^{1/3} Z^{7/3}\frac{e^2}{a_o}. \tag{1.8}$$

This is a famous power law – the 7/3 power of Z for atomic binding energies – going back to Milne [3] in 1927. Of course, screening of the potential $-Ze^2/r$ has to be introduced in 'real' atoms, and this reduces the coefficient $(3/2)^{1/3} \simeq 1.1$ in Eq. (1.8) to 0.77 in Milne's (self-consistent field) result.

With these two somewhat elementary examples to point a direction, let us turn next to a central potential $V(r)$ of a more complex form, that was used in early work on the electronic magic numbers in almost-spherical Na clusters [4]. The inhomogeneous electron density in such clusters is, of course, in this model, generated by the chosen one-body potential $V(r)$.

II. THE WOODS-SAXON POTENTIAL ESPECIALLY FOR ELECTRON LIQUID IN Na CLUSTERS

The Woods-Saxon potential has the form

$$V_{WS}(r) = \frac{-V}{1 + \exp[(r - \rho)/a]} \tag{2.1}$$

which is evidently a three-parameter function ($V, \rho,$ and a). As we will make use of the WKB approach in this and the following sections, we summarize here its basic elements. The WKB expression [5]

$$\int_{r1}^{r2} [2(E - V(x))]^{1/2} dx = (I + 1/2)\pi \tag{2.2}$$

where I is an integer, determines the (approximate) bound state eigenvalues E for a potential $V(x)$. (As is known, for the case of the Coulomb potential, the above expression gives the exact eigenvalues for the bound states with $I = (n - l - 1)$ and $V = V_{eff}(r) = -Z/r + (l + 1/2)^2/2r^2$, where the second term represents the 'centrifugal barrier', incorporating Langer's 'correction' of $l(l+1) \to (l + 1/2)^2$). In the case of the Woods-Saxon potential, the burden of the argument below – now semiclassical in nature since the exact eigenvalue spectrum of Eq. (2.1) has to be determined by numerical solution of Schroedinger's equation for eigenfunctions $\psi_{nlm}(r)$ and corresponding eigenvalues ε_{nl} – is to exhibit, first of all, an approximate scaling law for the WKB eigenvalue sum for magic numbers: $E_s^{WKB}(V, \rho, a)$. Essentially, one replaces sums over WKB eigenvalues by integration (in the sense of the Euler-Maclaurin summation formula), and this suggests, after some further simplification, that one should plot the WKB eigenvalue sum E_s in units of V against the magic numbers. The result[1] is shown in Figure 1. For $V = 0.218$ a.u. used in Ref. [4], the plot is largely linear, with the approximate fitting form

$$\frac{E_s}{V} = 0.54318N - 0.69972 \qquad (2.3)$$

However, when V is increased to twice this value (0.436 a.u.) corrections are needed to the linear form (2.3). We have also plotted, in Figure 2, the eigenvalue sum for a number of values of N, and the

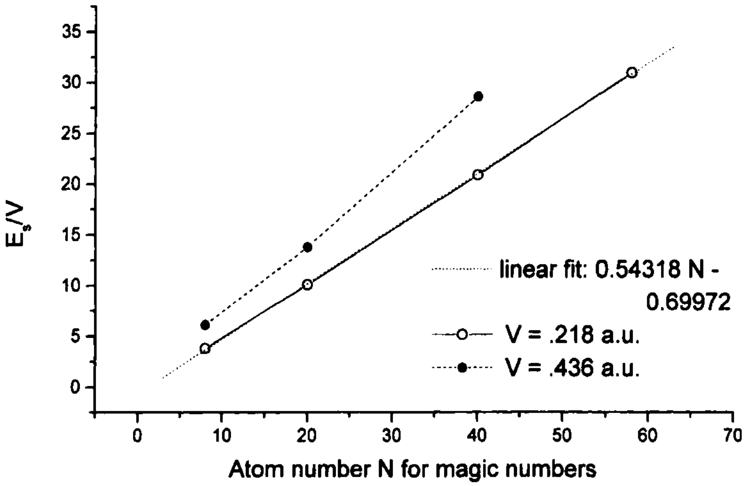

FIGURE 1 WKB eigenvalue sum E_s in units of V for the Woods-Saxon potential (2.1) as calculated for the two values of V recorded on the figure. The smaller of these was the value chosen in Ref. [4]; their values of $\rho = 3.93\,N^{1/3}$ a.u. and $a = 1.5$ a.u. were also used in constructing this figure. Note the remarkable linearity for the smaller value of V.

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[1] We note that in our treatment here of the Woods-Saxon potential, the Langer 'correction' is *not* used.

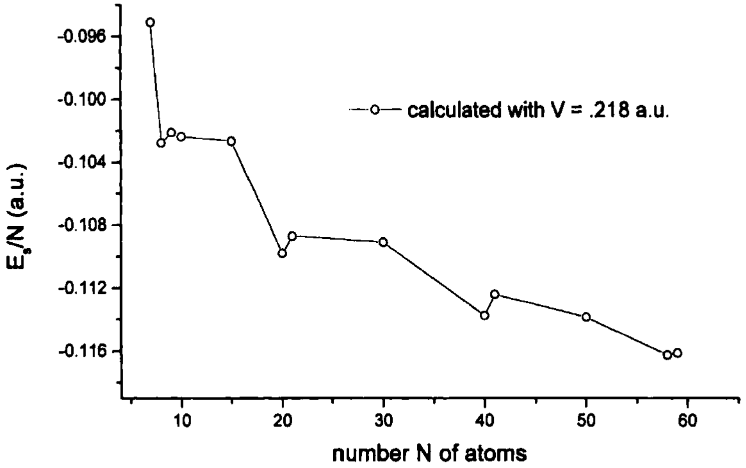

FIGURE 2 The WKB eigenvalue sum per atom, E_s/N, plotted *versus* the number of atoms N for the Woods-Saxon potential (2.1), with $V = 0.218$ a.u., and ρ and a taken as for Figure 1. The magic numbers obtained by Knight *et al.* [4] for Na clusters at 8, 20, 40, and 58 by numerical solution of the Schroedinger equation are quite evidently correctly reproduced using the WKB semiclassical approximation (2.2).

magic numbers are clearly seen at 8, 20, 40 and 58. Though Figure 2 involves the WKB approximation, these are the 'exact' values obtained for the magic numbers in Ref. [4] by direct numerical solution of the Schroedinger equation.

III. THE TRUNCATED COULOMB POTENTIAL: ELECTRON LIQUID IN FULLERENE

Our second example of magic numbers in an electron liquid relates to the so-called March model [6] of almost-spherical C cages. Here, we simplify by omitting self-consistency, as in the atomic case above, and consider, for example, C_{60} with the 'European football' shape of radius R, using the potential

$$\begin{aligned} V(r) &= -\frac{Ze^2}{R}, \quad r \leq R \\ &= -\frac{Ze^2}{r}, \quad r > R \end{aligned} \tag{3.1}$$

where Z has to be chosen as 60 to fully neutralize the 60 π-electrons which alone are treated by this model. For this case of the truncated Coulomb potential we have

$$\begin{aligned} V = V_{eff}(r) &= -Z/R + (l+1/2)^2/2r^2, \quad r \le R \\ &= -Z/r + (l+1/2)^2/2r^2, \quad r > R \end{aligned} \tag{3.2}$$

in Eq. (2.2), and we denote eigenvalues E by ε_{nl}. The turning points in this effective potential are then given by

$$r_1 = \frac{(l+1/2)}{Z\sqrt{2(\varepsilon_{nl}/Z^2) + (2/RZ)}} \tag{3.3}$$

and

$$r_2 = -\frac{Z}{2\varepsilon_{nl}} + \frac{1}{2Z}\sqrt{\frac{Z^4}{\varepsilon_{nl}^2} + 2\frac{(l+1/2)^2 Z^2}{\varepsilon_{nl}}} \tag{3.4}$$

where r_1 lies in the region $r < R$, and r_2 lies within $r > R$. In the present work we carry out the numerical solution of Eq. (2.2) for the eigenvalues ε_{nl}, for a range of values of Z and R.

Elsewhere, we have reported WKB eigenvalues for different values of Z and R. Here we emphasize the scaled result corresponding to Eq. (2.3) for neutral C cages. It should occasion no great surprise that $-Z^2e^2/R$ is the natural energy scale for sufficiently large R (see Fig. 3), and then Eq. (2.3) is replaced in the simple surface charge model by

$$E_s^{WKB} = -\frac{Z^2e^2}{R} f(Z^{1/2}R^{3/2}) \tag{3.5}$$

which is discussed briefly in the Appendix. The numerical findings are that, as the argument of the function f becomes large, $f \to 1$ (Fig. 4), while to regain, for neutral cages, the shape of Eq. (1.8), one must have

$$f(x) \propto x^{2/3} \quad \text{as } x \to 0, \tag{3.6}$$

leading to $E_s^{WKB} \propto Z^{7/3}$ as $R \to 0$.

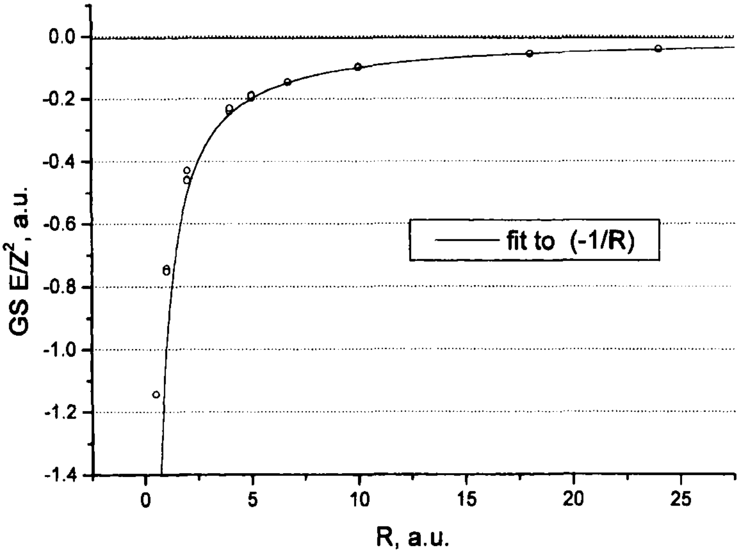

FIGURE 3 The WKB eigenvalue sum divided by Z^2 for neutral C cages, for the simple surface charge model represented by the truncated Coulomb potential (3.1). The fit to $-1/R$ is quantitative for $R \gtrsim 5$ a.u.

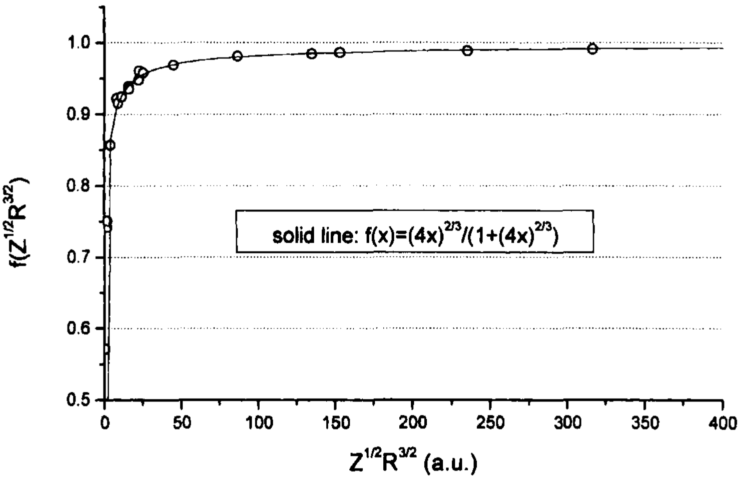

FIGURE 4 The 'scaling' function $f(Z^{1/2}R^{3/2})$ entering Eq. (3.5) *versus* its argument $Z^{1/2}R^{3/2}$. A useful approximate analytic fit embodying the limits $f(x) \rightarrow 1$ at large x and the scaling form (3.5) of $f(x)$ as $x \rightarrow 0$ is also shown in the solid curve.

IV. SUMMARY

The WKB method for calculation of eigenvalues in 'almost spherical' inhomogeneous electron liquids is not demanding numerically even for a potential such as that of Woods-Saxon form (Eq. (2.1)). Furthermore, it is shown here, by comparison with the exact numerical results of Knight *et al.* [4] for this potential, that the WKB eigenvalue sum correctly reproduces the magic numbers 8, 20, 40, 58 for almost-spherical clusters of Na atoms (see Fig. 1). As Figure 2 shows, for the choice of the potential strength $V = 0.218$ a.u. made by Knight *et al.* [4], at these magic numbers the WKB eigenvalue sum E_s^{WKB}, measured in units of V, depends linearly on the magic numbers. However, if V is doubled, corrections to the linear form are in evidence.

The second example is a simple surface charge model of almost-spherical C cages. Again, if a basic energy $-(Z^2e^2/R)$, with Z the positive charge on the cage ($+60\,|e|$ for fullerene) and R the radius of the 'European football', is used as the unit in which to measure the eigenvalue sum, a different, but again simple, scaling is in evidence.

These two non-trivial examples add to the successes of the semiclassical WKB method, which is frequently applied to simple standard models in quantum mechanics, and encourage, we feel sure, further related studies when a central potential $V(r)$ is a useful approximation for molecules (*e.g.*, UF_6) and clusters other than alkalis such as Na.

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APPENDIX: SIMPLEST DENSITY-FUNCTIONAL (LOCAL DENSITY OR THOMAS-FERMI) APPROXIMATION LEADING TO SCALING LAW OF THE FORM (3.5) FOR TRUNCATED COULOMB POTENTIAL MODEL OF NEUTRAL ALMOST-SPHERICAL C CAGES

The original density-functional theory is the Thomas-Fermi statistical method [7,8]. This is fundamentally based on the constancy of the chemical potential μ throughout the inhomogeneous electron cloud of electron density $\rho(\mathbf{r})$ in the atom, molecule or cluster under consideration. As set out in, for example, Ref. [5],

$$\mu = \left(\frac{1}{2m}\right)\left(\frac{3h^3}{8\pi}\right)^{2/3}[\rho(\mathbf{r})]^{2/3} + V(\mathbf{r}) \tag{A1}$$

and solving for the density $\rho(\mathbf{r})$ yields the (local) density-potential relation of the Thomas-Fermi statistical method as

$$\begin{aligned} \rho(\mathbf{r}) &= const.\ [\mu - V(\mathbf{r})]^{3/2} \quad \mu - V(\mathbf{r}) > 0 \\ &= \text{o} \quad \text{otherwise.} \end{aligned} \tag{A2}$$

If we now insert the truncated Coulomb potential (3.1), used in the main text to model almost-spherical carbon cages, then μ can be determined as a function of Z and cage radius R by using the density normalization condition

$$\int \rho(\mathbf{r})d\mathbf{r} = Z \tag{A3}$$

for neutral C cages. One is led then from Eqs. (A2), (A3), and (3.1), after some manipulation, to a scaling property (compare Eq. (3.5)), that $\mu \sim -Ze^2/R$ times a function of $Z^{1/2}R^{3/2}$. Adding the intuitive reasoning that the eigenvalue sum must be of the order of the number of electrons (Z for neutral cages) times the chemical potential μ leads directly to the (of course) approximate scaling relation (3.5).

It only remains to comment on the connection between the semiclassical Thomas-Fermi method and the WKB approximation, the latter again having its roots in semiclassical theory. While the WKB eigenvalues are discrete, as are the correct Schroedinger energy levels, for atoms, molecules and clusters, the Thomas-Fermi approximation to the total energy is more drastic, replacing the summation over discrete WKB eigenvalues by an integration out to the chemical potential μ over a continuum with an appropriate semiclassical electronic density of energy states.