Nuclear shell model applied to metallic clusters

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Abstract. We apply the nuclear shell model to jellium clusters of up to twenty-one Na atoms. Binding energies, ionization potentials, and photoabsorption cross sections are calculated and compared with mean-field results.

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1. Introduction

We study sodium clusters in the jellium approximation, where the ionic cores form a uniform positive background of spherical shape. Heretofore this model has been applied through the techniques of the local-density approximation (LDA) [1] and the local-spin-density approximation (LSDA) [2]. We adopt another approach: diagonalizing the jellium Hamiltonian by the techniques of the nuclear shell model (SM). For comparison we make LSDA computations for the same system. No detailed comparison with experiments has been made since the spherical jellium model cannot give the correct description of small clusters with the accuracy of the methods of quantum chemistry [3].

2. Many-body shell model of atomic clusters

Deduced from bulk sodium, the radius of the jellium sphere is \( r_c = 3.93a_0N_a^{1/3} \), with \( a_0 \) the Bohr radius and \( N_a \) the number of atoms. Each valence electron possesses then a potential energy due to the jellium background given by

\[
V(r) = \begin{cases} 
\frac{N_e e^2}{4\pi\varepsilon_0} \left( \frac{r^2}{r_c^2} - 3 \right) & \text{for } r \leq r_c, \\
-\frac{1}{r} & \text{for } r > r_c.
\end{cases}
\]

Since the valence electrons also feel their mutual Coulomb repulsion, the total many-body Hamiltonian for \( N_e \) valence electrons is

\[
H = \sum_{i=1}^{N_e} \left[ -\frac{\hbar^2}{2m} \nabla_i^2 + V(r_i) \right] + \frac{1}{4\pi\varepsilon_0} \sum_{i<j} \frac{e^2}{|r_i - r_j|}.
\]

In a SM calculation we first choose a finite orthonormal set of single-electron (s.p.) states. Then the Hamiltonian (2) is diagonalized in the complete, or possibly in a restricted, space of antisymmetric many-particle states constructed from the s.p. states. We have modified the SM code OXBASH [4] so that it works in LS coupling.

Our s.p. basis consists of harmonic oscillator (HO) wave functions, with spin, for the orbits 1s, 1p, 1d\(2s\), 1f\(2p\), 1g\(2d\)\(3s\), 1h\(2f\)\(3p\), which comprise 112 states in all. In this s.p. basis we can make complete SM calculations only for the smallest clusters. So we need a proper technique to pick the most important many-particle basis states out of the complete SM space.

The truncation is done in terms of HO configuration energies. For bookkeeping, we write the HO s.p. energies as \( \epsilon(1s) = 0 \), \( \epsilon(1p) = 1 \), \( \epsilon(1d\,2s) = 2 \) etc. Thus, for example, for \( N_a \) the lowest configuration of symmetry \( L = 0 \), \( S = 0 \), \( \pi = + \) is \( 1s^2 \, 1p^6 \) and has energy 6. We then label the degree of truncation by \( n = 0, 2, 4, \ldots \) (parity conservation excludes odd values) according to configuration energy, so that in our example a calculation of accuracy \( n \) means diagonalization of the Hamiltonian (2) in the space of many-particle HO states of energy \( \leq n + 6 \). In the case of \( N_a \) states of symmetry \( L = 1 \), \( S = 0 \), \( \pi = - \), accuracy \( n \) means a cutoff value of \( n + 7 \), since the lowest configuration energy for this symmetry is 7.

The HO basis functions contain one parameter, the oscillator length \( b \), which we determine by minimizing the ground-state energy.

3. Results

3.1. Ground-State Energies

The basic quantity to calculate for a cluster is its ground-state energy. With an increasing accuracy index \( n \), this
energy decreases and converges towards the value of an exact SM calculation in our s.p. basis.

In Fig. 1 we depict for sodium clusters the binding energy per atom as calculated on the SM and in the LSDA. For \( N_a = 1-3 \) we have performed complete SM calculations. For \( N_a = 4-5 \) we have done \( n = 10 \) calculations, which still to a very high accuracy correspond to complete calculations. We note that the LSDA results agree with the SM ones, which proves the accuracy of the LSDA. In fact, we expect that the LSDA becomes even more accurate with increasing cluster size, since it is exact in the infinite limit.

For \( N_a = 6-8 \) we have performed \( n = 6 \) calculations and for \( N_a = 9-10 \) only \( n = 4 \) calculations. These calculations are no longer good approximations to complete calculations in our basis. This is demonstrated in Fig. 2, where we show the binding energies of \( N_a \) as obtained with different \( n \) values. Comparison of the Hartree-Fock energy \(-1.27 \text{ eV} \) [5] with our \( n = 0 \) result shows that the HO s.p. states are near optimum.

3.2. Ionization potentials

Figure 3 shows the ionization potentials for sodium clusters of \( N_a = 2-10 \). We see that the SM and LSDA results coincide almost exactly for \( N_a \leq 5 \), and we know that the SM results are very reliable in this range. For \( N_a \geq 6 \) they still closely parallel each other.

Secondly we observe that, although the theories do yield the correct average value of roughly 4 eV, they fail to reproduce the rather regular odd-even staggering evident in the experimental curve [6]. This is to be expected since the Hamiltonian (2) with its long-range repulsive interaction does not yield any pairing like that in nuclei. In clusters, the odd-even staggering is caused by the Jahn-Teller effect [7], i.e. deformation of the ionic background away from spherical shape.

3.3. Photoabsorption

For atomic clusters the photoabsorption cross section consists predominantly of E1 excitation. The area of a single excitation peak is found by the relation

\[
\int_{\Delta \lambda} \sigma(\lambda) \, d\lambda = \frac{8 \pi^3 a_0 \hbar c}{3} \frac{1}{E_{f_i}} \frac{1}{(2L_i + 1)(2S + 1)} \sum r || L_i S ||^2, \tag{3}
\]

where the triple-barred matrix element is reduced with respect to \( L \) and \( S \).