TOTAL ENERGIES, ABUNDANCES, AND ELECTRONIC SHELL STRUCTURE OF LITHIUM, SODIUM, AND POTASSIUM CLUSTERS

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The total energies of lithium, sodium, and potassium clusters are computed as a function of N, the number of atoms in a cluster, using a jellium local-density-functional scheme. The calculated binding energy change shows discontinuities at certain cluster sizes because of the existence of electronic shell structure. This is consistent with the abundance discontinuities found in the mass spectrum for sodium. Predictions of the mass spectra are made for lithium and potassium clusters. The ionization energies for individual clusters are calculated and these also show shell structure.

IT HAS BEEN REPORTED RECENTLY[1] that the mass spectrum of metal clusters produced in a supersonic expansion of sodium vapor contains large peaks or steps at 8, 20, 40, 58, and 92 atoms per cluster. This abundance curve (mass spectrum) was explained[1] by using model spherical potential wells for the sodium 3s valence electrons in each individual cluster. The bound electron states consist of a series of shells, and those clusters having enough electrons to fill these shells are more stable than other clusters. Here we use a jellium model to compute the shell structure and to relate the major features of the abundance curves to the total energy difference between clusters with different numbers of atoms. The features of the electronic shell structure are also apparent in the calculated ionization potential.

Realistic calculations of electronic properties and total energies for sodium metal clusters have been done for small clusters[2,3] (up to Na_8) using the pseudopotential approach and the density-functional scheme[4,5]. This approach is much more difficult for large clusters, hence we replace the real cluster by a jellium sphere surrounded by valence electrons. The calculations of the total energy are based on a self-consistent local-density-functional approach[6]. The fact that a nearly free electron model adequately describes the bulk properties of alkaline metals supports the concept that the detailed nature of the screened ion potential introduces only minor effects. Hence the jellium approximation, which smears out the ions in the cluster to form a uniform, positively charged sphere containing interacting electrons, is considered to be a good first approximation. This model preserves many of the physical characteristics of clusters, but it should not be valid for clusters with a small number of atoms where the atomic arrangement is important in determining the physical properties of the cluster.

For the total energy calculation, the electron-electron exchange-correlation energy functional is calculated using the spin-dependent functional form of Perdew and Zunger[7] which is based on the electron gas calculations of Ceperley and Alder[8]. The one-particle Kohn-Sham equation[5] is solved numerically by first using finite differences and matrix diagonalization, and secondly direct integration to get the self-consistent charge density.

Recently some properties of sodium clusters were calculated[9,10] using a similar model to that presented here. Although the two calculations[9,10] utilize different exchange-correlation energy functionals, the results for the ionization energies of the sodium spheres were similar. The abundance curves were not studied in these calculations and the relationship between the computed shell structure and the properties of real clusters was not discussed. Here we compare the total energies, ionization potentials, and related properties of clusters for lithium, sodium, and potassium within the jellium model. Although the energy spectra of these materials are very similar, some important differences appear because of the change in the jellium density.

For N atoms in a cluster, the radius of the uniformly charged sphere is taken as $N^{1/3}$ multiplied by r_s, the radius of the Wigner-Seitz cell in the bulk. For lithium, sodium, and potassium, we have r_s = 3.25 a.u., 3.93 a.u., and 4.86 a.u. respectively. The total energy of the system, E(N), is the sum of the

ion-ion interaction energy (approximated by the electrostatic self energy of the jellium sphere) and the electronic energy obtained from the density-functional scheme. The former is a smooth function of N, but the latter has discontinuities whenever shells are completely filled. The wavefunctions that form the set of solutions to the Kohn-Sham equation are labelled by the principal quantum number n (equal to one plus the number of nodes in the wavefunction), and by the angular momentum and spin quantum numbers l, m_l, and m_s. States with the same n and l values are degenerate because of the assumption of spherical symmetry; hence each shell has a $2(2l+1)$ degeneracy. Since there should not be any preferred direction for a free system, the average charge density, which is spherical, is used in the calculation of the open shell clusters.

In the local-spin-density calculation for partially filled shells, states with unpaired electrons have lower total energy because of the Pauli exclusion principle and the Coulomb interaction between electrons. However, in a real cluster the high l degeneracy does not exist. States with different m_l values are split, and it takes energy to promote the electrons to the higher levels needed to make a spin-polarized cluster. It is therefore difficult to determine the spin configuration for the ground state, hence the following calculation is performed for the non-spin-polarized case.

The binding energy E_B of a cluster of N atoms is defined as the negative of the energy difference between that of the cluster, $E(N)$, and that of N free atoms:

$$E_B(N) = -[E(N) - NE_a], \qquad (1)$$

where E_a is the energy of the atom. The binding energy change between two clusters can be written as

$$E_B(N+1) - E_B(N) = E(N) + E_a - E(N+1). \qquad (2)$$

If eq.(2) is positive, an N+1 cluster is favored over an N cluster plus a free atom. To evaluate eq.(2), we need to know the energy of an atom as a reference state. To avoid this, we define

$$\delta(N) = [E_B(N) - E_B(N-1)] - [E_B(N+1) - E_B(N)]$$

$$= E(N+1) + E(N-1) - 2E(N). \qquad (3)$$

where $\delta(N)$ is a relative binding energy change for clusters with N atoms compared to clusters with N+1 and N-1 atoms. It is independent of the reference energy of free atoms. If, at a certain N, a level is just filled and the next available level is separated from the filled level by an energy gap, the total cluster energy will have a jump from $E(N)$ to $E(N+1)$. This gives rise to a peak in $\delta(N)$. A peak in $\delta(N)$

indicates that a cluster with N atoms is relatively stable, and this cluster should have a larger abundance in the mass spectrum than a cluster with N+1 atoms.

In Fig. 1, the calculated $\delta(N)$ for lithium, sodium, and potassium is shown for N up to 95; the filled orbitals are also marked. The peaks for sodium (Fig. 1(b)) appear at N = 8, 18, 20, 34, 40, 58, and 92. In this calculation, the energy levels of the 2d, 3s, and 1h levels are very close, so that the peaks at N = 68 and 70 found in the spherical potential well calculation[1] do not appear. This is consistent with the experimental data. The peak at N = 18, which is not apparent in the measured mass spectrum, is close to the peak at N = 20, but the latter is much higher. This may be responsible for the rise in the experimental counting rate at N = 18, which drops only after N = 20. Otherwise, except for the peak at N = 34, all the structure found in this calculation is consistent with the experimental mass spectrum. The gap between the 1f and 2p levels (at N = 34) is apparently overestimated in the jellium calculation.

For lithium and potassium (see Fig. 1(a) and (c)), the peaks are at the same positions, except that only a small step appears at N = 40 in potassium. Moreover, the magnitude of the peaks decreases
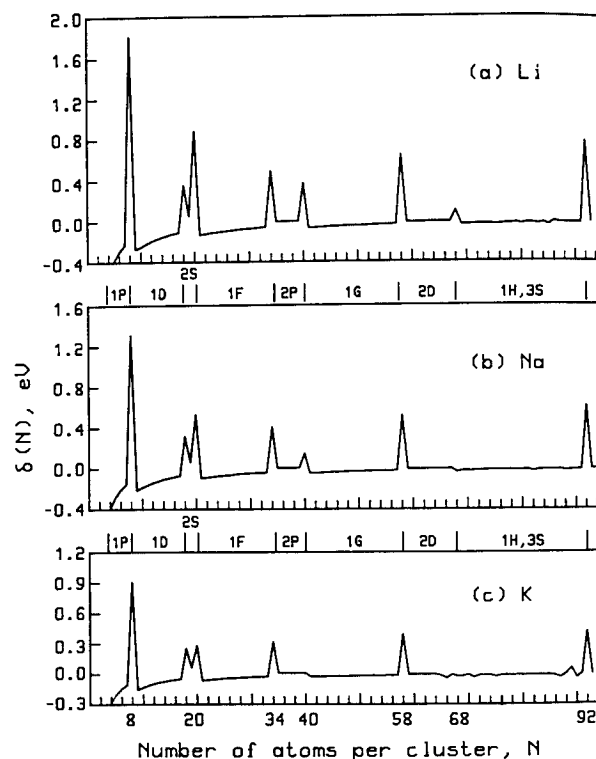

Fig. 1. The relative binding energy change $\delta(N)$ (see text) versus N for (a) lithium, (b) sodium, and (c) potassium. N is the number of atoms in a cluster. The labels correspond to filled shell orbitals.

from lithium to potassium. This can be understood by examining the one-electron effective potential, which is plotted in Fig. 2 for the $N = 40$ clusters of lithium, sodium, and potassium. The radii of the
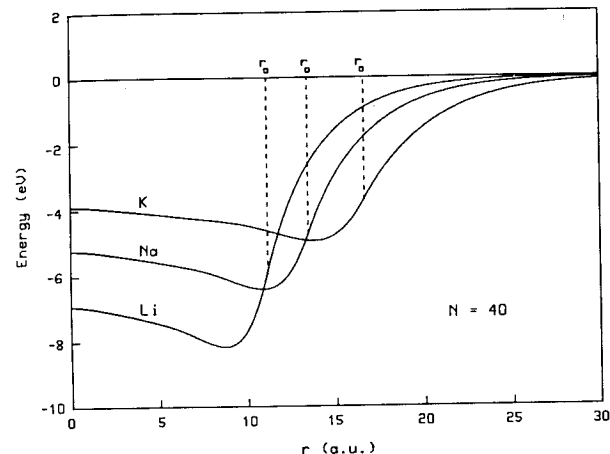

Fig. 2. The effective radial electronic potential of a jellium sphere with 40 atoms for lithium, sodium, and potassium. The radii of the jellium spheres are given.

jellium spheres are scaled with r_s; the difference in depths comes from the fact that the smaller the radius of a uniformly charged sphere, the deeper the electrostatic potential for the electrons inside the sphere. The average depths of the wells in Fig. 2 are close to the sum of the bulk Fermi energy, 4.72 eV (3.23 eV, 2.12 eV)[11], and the experimental work function, 2.32 eV (2.7 eV, 2.39 eV)[12], for lithium (sodium, potassium). This illustrates how some bulk properties can determine the properties of the clusters. Because the effective potential is shallower in potassium, the spacing between the energy levels is smaller, and hence the gaps are smaller. We therefore expect that the gross features in the mass spectrum might be less distinct in potassium than in sodium. The reduction of the peak at $N = 40$ in potassium also arises because of the change in r_s. Some of the eigenvalues for $N = 40$ are plotted in Fig. 3 as a function of this parameter. As r_s gets larger, the gap between the 2p and 1g levels gets smaller, and almost vanishes at the potassium r_s value. Hence we expect the potassium mass spectrum to have at most a small discontinuity at $N = 40$.

The complete explanation of the mass spectra requires a theory beyond this purely static description. An understanding of the kinetics of the cluster formation, including the "fission" and "fusion" rates of clusters, is required. We also need to consider the experimental conditions, e.g., the adiabatic expansion, and the ionization process (including the wavelength dependence and the possible cluster fragmentation). Those have been checked and are not responsible for the peaks or discontinuities in the

mass spectra[1]. The results of these total energy calculations agree with the occurrence of sharp discontinuities in the mass spectrum of sodium clusters and provide a model for the energetics.
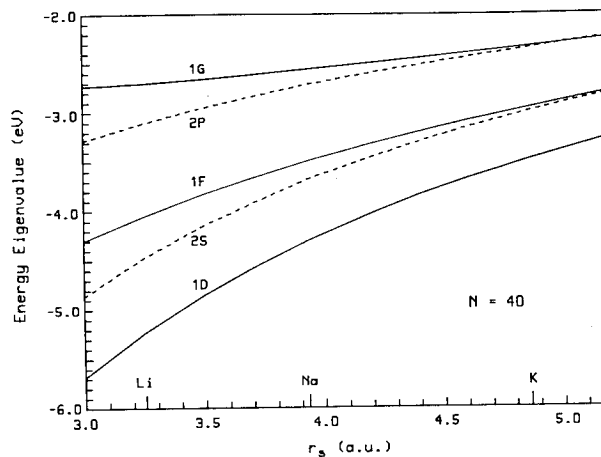

Fig. 3. The electron eigenvalues of a jellium sphere with 40 atoms is plotted as a function of r_s. The levels with the quantum number $n = 1$ (2) are plotted with solid (dashed) lines. The 2p level is just filled for $N = 40$.

Another physically measurable quantity which could further explore the role of the electronic shell structure of the clusters is the ionization potential. This quantity can be calculated from the total energy difference between a neutral and a singly ionized cluster. In Fig. 4 we plot the N dependence of the ionization potentials for lithium, sodium, and potassium. Discontinuities appear at the same positions
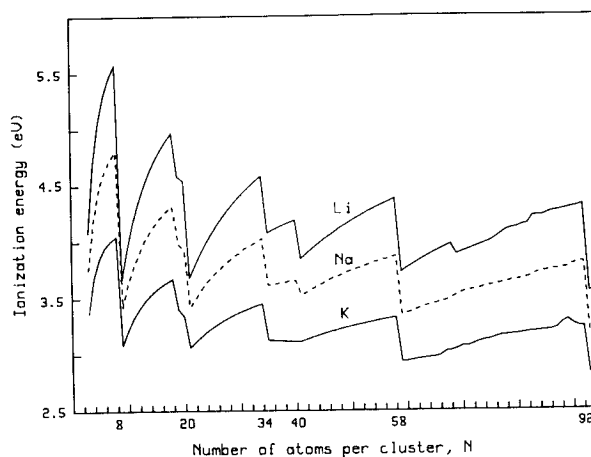

Fig. 4. The ionization potentials calculated for jellium spheres as a function of N for lithium (solid line), sodium (dashed line), and potassium (solid line). N is the number of atoms in a cluster. The calculated work functions of the infinite half plane jellium surface for lithium, sodium, and potassium are 3.37, 3.06, and 2.74 eV respectively[12].

as in Fig. 1. The increase of the ionization potential with N within a shell is explained by Ekardt[10] as a result of the exchange-correlation enhancement. The ionization energy should approach the work function of the infinite half plane as N increases. The calculated work functions of the infinite flat jellium surface for lithium, sodium, and potassium are 3.37, 3.06, and 2.74 eV respectively[12]. We have observed this overall decreasing trend, but the convergence is slow in all cases. Experiments measuring the photoionization potentials have been performed for clusters with N from 1 to 15 and N = 19, 35, 55, 65 [13]. The data for N from 1 to 15 do not show any noticeable shell structure and we are unaware of any published experimental data for contiguous values of N above 15.

Although more realistic atomic potentials and structures for large clusters can provide more detailed information on the electronic and structural properties of clusters, this simple model does give both qualitative and quantitative information. If a jellium ellipsoid model were used instead of a sphere, the $2(2l+1)$ degenerate energy levels would split into a series of levels with two-fold $(m_l = 0)$ and four-fold $(m_l \neq 0)$ degeneracy. Unless the deformation from a sphere is large, it is not expected that the

features in the shell structure would change greatly.

In conclusion, we have calculated the total energies for metal clusters of lithium, sodium, and potassium using a jellium sphere model and the local-density-functional formalism. The total energy as a function of cluster size has discontinuities because of the existence of electronic shell structure. The corresponding shell closing numbers are consistent with the positions of steps or peaks in the mass spectrum of sodium. The results of the model for potassium are very similar to those for lithium and sodium, except that the shell closure at N = 40 does not give rise to a jump in the total energy. The ionization potentials for these clusters are also calculated. Measurements of this property could give useful information concerning the role of shell structure.

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