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**Pseudopotential Calculation of the Total Energy of Small Sodium Clusters: Cross-Over from Electronic-Closed Shell to Geometrical-Structure Stability**

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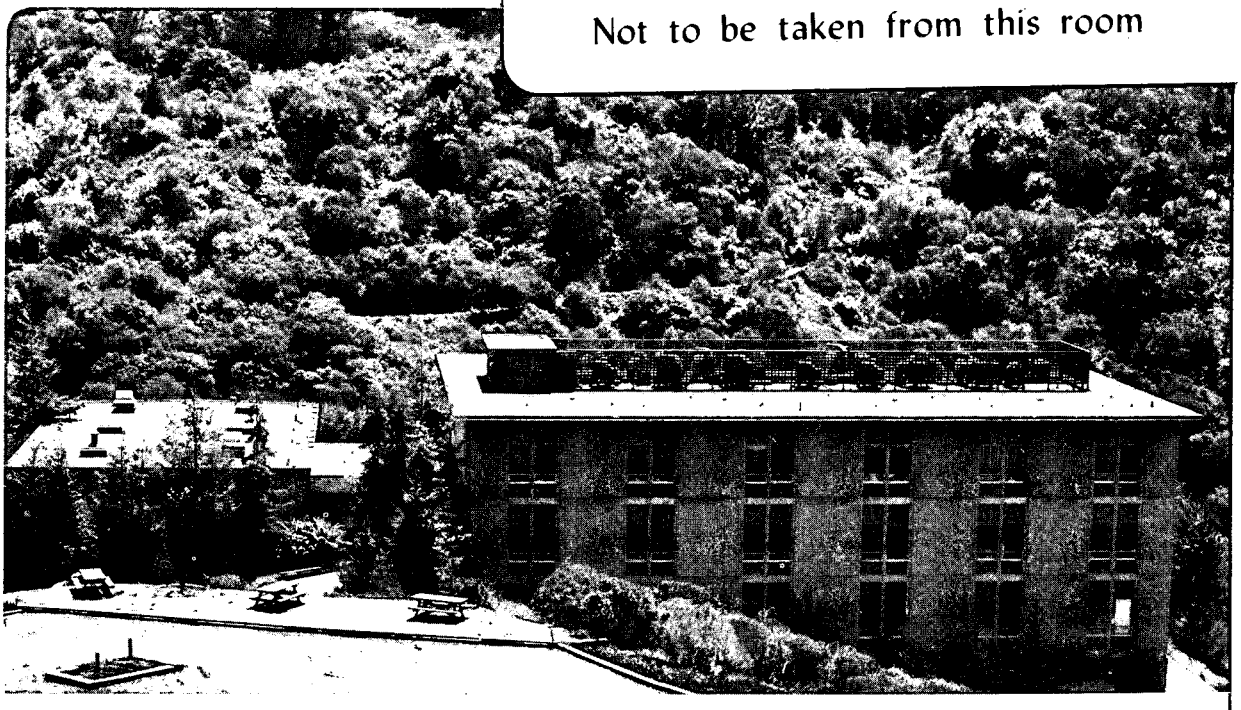

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# PSEUDOPOTENTIAL CALCULATION OF THE TOTAL ENERGY OF SMALL SODIUM CLUSTERS: CROSS-OVER FROM ELECTRONIC-CLOSED-SHELL TO GEOMETRICAL-STRUCTURE STABILITY

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## Abstract

A pseudopotential calculation of the total energy of small sodium clusters is presented. It is based on a local-pseudopotential scheme and local-density correlation and exchange. It includes a spherical distribution of electronic charge and minimizes the energy with respect to the position of the ions. It is found that the most stable clusters are (1) those that correspond to closed electronic shells for clusters with fewer than approximately 100 atoms; and (b) those that correspond to geometrical polyhedral clusters for numbers larger than that. A cross-over between electronic-level dominance and geometrical-structure stability, found experimentally at larger numbers, is thus theoretically established.



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## I. Introduction

Ever since the discovery by Knight *et al.*[1] of quantal shell structure in small droplets of sodium metal, with characteristic "magic numbers", cluster physics has become an active field of theoretical and experimental investigation. Many properties of a large variety of clusters have been examined[2] -- mass abundance spectra, fragmentation spectra and binding energy, supershell structure[3], ionization potential, photoelectron spectra and electron affinity, static electric polarizability[4], plasma resonance spectra, and thermal properties[5], to name a few. Because a cluster lies somewhere between a solid and a molecule, the problem has been approached from two extreme directions -- solid-state theorists employ modified quantum models of bulk solid[2,6,7], whereas molecular chemists and atomic physicists attempt molecular dynamical calculations in which one builds up clusters atom by atom. A compelling stimulus throughout has been the desire to understand how an extended crystalline solid develops from growing cluster aggregates. Two major experimental results in this regard have been (i) the observation of cluster stability exactly at the so-called electronic magic numbers[1,8-11]-- which correspond to electronic shell-closings -- for cluster sizes less than 200 , and (ii) the more recent discovery by Martin *et al.*[12] of cluster-stability at magic numbers corresponding to closed-packed atomic shell arrangements in icosahedral or cuboctahedral packings for clusters of size between ~ 1,500 and 22,000. The stability characteristics of the small clusters are well supported by the

calculations of Cohen *et al.*[13] and of Ekardt[14], based on the self-consistent jellium background model (SJBM). Although jellium-like mean-field calculations exist for cluster-sizes of the order of several hundred[15], in order to study properly this transition in stability from electronic to atomic magic numbers, one needs to incorporate the atomic structure, *i.e.* the ions must be explicitly included for any cluster-size. One would, in principle, like to approach the problem by self-consistently determining atomic configurations and the associated electronic charge density that yield the minimum total energy for each cluster size in question. Several systematic methods have been developed in this regard by solid-state theorists[6] and molecular chemists[16]. Unfortunately, because of the enormous computational tax, these calculations as of now are limited to sizes well below a hundred ions. Work has also been done on statistical descriptions of the electronic level structure[17] and the asymptotic size-dependence of the energy in large clusters[18]. However, no successful theory of the observed transition from electronic to atomic dominance in the structure have appeared in print, as far as the authors are aware.

The present contribution attempts to study these clusters by means of a pseudopotential approach, for which one can easily tackle clusters of size up to a few thousand with reasonable computational effort. By comparing the numerical results for total energy per atom obtained at several electronic and atomic magic numbers, a pattern emerges which clearly shows that for small clusters the electronic structure dominates, whereas at larger sizes the closing of ionic crystal-like shells becomes paramount. A cross-over is thus found. It should be pointed out that in all cases the clusters are small, in the

traditional sense of the concept, since all atoms are, in all cases, within a few Ångstrom from the surface, *i.e.* far away from what can be considered the bulk limit.

Section II describes the model in detail, section III contains the results for the electronic charge density and total energy for cluster sizes corresponding to several electronic and atomic "magic numbers" and section IV includes a discussion and summary.

## II. The model

The model consists of approximating the self-consistent Kohn-Sham (KS) potential observed by each electron with an infinite well, the shape of whose boundary is defined, in principle, by the surface of the outermost ions in the cluster. Because of the observation that the spherical jellium model works well for small clusters ($N < 200$), coupled to the convenience of separability of co-ordinates in a spherical geometry, the electron confining regions for any cluster-size are taken to be infinite spherical wells. Two different schemes of choosing the cluster sizes for the purpose of calculation are considered, in conformity with the spherical boundary :

(A) The clusters representative of the geometrically closed shells of atoms (hereafter described as the ones with **atomic** magic numbers) are made up of finite, perfect periodic lattices cut off by the surface of the spherical well and then allowed to relax; and

(B) The clusters representative of **electronic** magic numbers consist of the ions placed within the electron confining spherical well so as to minimize (numerically) the total energy of the cluster.

For the atomic magic number structures four different types of finite lattices have been considered in this calculation :

(A1) Finite body-centered-cubic (*bcc*) lattices (the bulk structure of sodium at low temperatures) with an atom at the center of the electron confining sphere;

(A2) Finite face-centered-cubic (*fcc*) lattices with the sphere centered at an atom in the lattice (henceforth referred to as *Type-I fcc* clusters);

(A3) Finite *fcc* lattices with the sphere centered at the center of a conventional unit cube (referred to hereafter as *Type-II fcc* clusters) and,

(A4) Finite *fcc* lattices with the sphere centered at the center of a tetrahedron of nearest-neighbor atoms (*Type-III fcc* clusters).

Each type of cluster, initially arranged according to schemes (A1-4) and (B) described above, correspond to different distributions of atoms in the sphere and, accordingly, yield separate sets of magic numbers. There are a few numbers that are common to two or more cluster types, *e.g.* 68, which is common to schemes (A3), (A4) and (B), and 92, common to schemes (A4) and (B).

All schemes (A1-4) and (B) are starting points for relaxing the structures in search of an energy minimum. The relaxation is such that certain constraints, listed below, are obeyed.

(1) No two ions lie within a distance $2r_c$ of one another, $r_c$ being the effective 'hard-core' radius for the metallic ion under consideration, *i.e.* sodium. One could estimate $r_c$ from the effective two-body interaction between two sodium atoms in a lattice obtained by second-order perturbation theory of the pseudopotential[19]. In this way, $(2r_c/a)$ has been estimated[20] to be $\sim 0.82$, where $a=4.225$ Å is the bulk lattice-constant for sodium in the *bcc* structure.

(2) No ions should lie outside the effective jellium surface, a sphere of radius $R_+$.

(3) The jellium (uniform positive-charge background) sphere, of radius $R_+$ lies inside the infinite spherical well that confines the electrons; the latter has radius $R$. The difference in radii $\delta = R - R_+$ physically represents the 'decay length' of electronic wave-functions outside the actual surface of a solid or cluster, which is bound by a *finite* potential well. The value of $(\delta/a)$ is taken to be a constant, equal to $0.29$, independent of cluster size. This is a very good approximation[21], as seen from the SJBM results of Ref. 14.

Lattice relaxations that obey the above constraints are allowed on the way to finding the lowest energy states of the various clusters.

Several comments are relevant :

(1) The electronic charge-density calculated here is not far from that calculated by SJBM. A direct comparison of the graphs in Figure 1

with counterparts of those in Figure 3 of Ref.14 makes this fact apparent.

(2) The modification of the electronic wave-function at the ionic sites is taken into account in the first-order perturbation of the pseudopotential. Any higher-order perturbation, which is computationally forbidding, should have (for alkali-atom clusters) an insignificant effect on the trend of results for the total energy.

The total energy $E_{tot}$ per atom, in the model considered here, is a sum of several contributions given by:

$$E_{tot} = E_{el\text{-}el} + E_{el\text{-}ion} + E_{ion\text{-}ion} + E_{kin} + E_{xc} \quad . \qquad \text{(II.1)}$$

The various terms on the right hand side of the above equation are self-explanatory and are calculated for a cluster of size $N$ using the following formulas :

For the electron-electron Coulomb interaction

$$E_{el\text{-}el} = N \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\, \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}\, d\mathbf{r}' \quad ; \qquad \text{(II.2)}$$

for the electron-ion Coulomb interaction

$$E_{el\text{-}ion} = - e^2 \sum_i \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_i|} \, d\mathbf{r} + E_{ps}^{(1)} \quad , \qquad \text{(II.3)}$$

where $E_{ps}^{(1)}$ is defined below; the ion-ion Coulomb interaction

$$E_{ion\text{-}ion} = \frac{e^2}{2N} \sum_{i \neq j} \frac{1}{|\boldsymbol{R}_i - \boldsymbol{R}_j|} \quad ; \tag{II.4}$$

for the electron kinetic energy

$$E_{kin} = -\frac{\hbar^2}{2mN} \sum_{\alpha,\sigma} \int \psi^*_{\alpha\sigma}(\boldsymbol{r})\, \nabla^2\, \psi_{\alpha\sigma}(\boldsymbol{r})\, d\boldsymbol{r} \quad ; \tag{II.5}$$

and for the electron exchange and correlation energy in the local-density approximation

$$E_{xc} = \int d\boldsymbol{r}\, \rho(\boldsymbol{r})\, \varepsilon_{xc}(\rho(\boldsymbol{r})) \quad . \tag{II.6}$$

In equations (II.2-6) $\psi_{\alpha\sigma}(\boldsymbol{r})$ stands for the wave-function of the electron in the quantum state $\alpha$ with spin $\sigma$. Also introduced above are the electronic number density $\rho(\boldsymbol{r})$ normalized to one,

$$\rho(\boldsymbol{r}) = \frac{1}{N} \sum_{\alpha,\sigma} |\psi_{\alpha\sigma}(\boldsymbol{r})|^2 \quad , \tag{II.7a}$$

$$1 = \int d\boldsymbol{r}\, \rho(\boldsymbol{r}) \quad ; \tag{II.7b}$$

the first-order pseudopotential contribution $E_{ps}^{(1)}$ is

$$E_{ps}^{(1)} = \sum_i \int d\boldsymbol{r}\, \rho(\boldsymbol{r})\, V(|\boldsymbol{r} - \boldsymbol{R}_i|) \quad , \tag{II.8a}$$

with the local pseudopotential function $V(r)$ given by[22]

$$V(r) = \frac{e^2}{r_0} u, \qquad r < r_0 \quad ,$$

$$- \frac{e^2}{r} , \qquad r > r_0 \quad , \tag{II.8b}$$

where $u$ and $r_0$ are phenomenological parameters;

and the exchange-correlation local density functional is

$$\varepsilon_{xc}(\rho(\mathbf{r})) = - 0.9162/r_s(\mathbf{r}) - 0.0666\ G[r_s(\mathbf{r})/11.4] \quad , \tag{II.9}$$

where the quantity $r_s(\mathbf{r})$ and the function $G$ are given by[14] :

$$r_s(\mathbf{r}) = \frac{1}{a_B} [3/4\pi\rho(\mathbf{r})]^{1/3} \quad ,$$

and where $a_B = 0.529\ \text{Å}$ is the Bohr radius, and

$$G(x) = \left[ (1 + x^3) \ln \{1 + \frac{1}{x}\} - x^2 + \frac{x}{2} - \frac{1}{3} \right] \quad .$$

The values of the pseudopotential parameters $u$ and $r_0$ are taken from the results known[22] in the thermodynamic limit:

$u = - 0.3632\ Ry$, and $r_0 = 1.097\ \text{Å}$

respectively. The only difference between the small clusters and the bulk arises from the drastic changes in the electronic charge densities.

## III Calculations and results

For clusters corresponding to electronic magic numbers there is complete spherical symmetry in the charge density of the electrons *i.e.* $\rho(\mathbf{r})$ is only a function of $r=|\mathbf{r}|$. This simplifies the computation enormously, because the integrals in (II.2) and (II.3) now get reduced respectively to one and two-dimensional integrals. A further considerable reduction in computational effort occurs in the calculation of $E_{el\text{-}ion}$ when one relaxes the ion positions (in any scheme) against the stationary spherically symmetric electronic background to get to the lowest energy configuration. Unfortunately the charge density arising from electrons at the outermost -- partially filled -- shell (*i.e.* the Fermi level) does not possess a complete spherical symmetry for clusters with numbers other than the electronic magic numbers, including the atomic magic numbers. However, simple electrostatic considerations show that, for large $N$, the correction to the total energy per atom, if one symmetrically averages over all electron states at the Fermi level in configurations with partially filled outer electronic shell, can be easily estimated. It is of the order of $\Delta E_{el\text{-}el} \sim 0.1(n/N^2)E_{el\text{-}el}$, as seen in the Appendix; here $n$ is the smallest of the numbers of filled and unfilled states in the shell at the Fermi level. In most situations $n \ll N$, and spherical averaging over all states at the Fermi level involves errors which are always tolerable and usually very small. The calculations were therefore performed with spherically averaged charge distributions.

Tables 1 and 2.1-2.4 respectively display results for the various components of energy and the total energy per atom for a set of magic numbers corresponding to filled electronic and atomic shells for the different cluster types considered here.

Figure 2 graphically displays the results for the total energy per atom as a function of $N$ for both electronic and atomic magic numbers. The convex hulls of lowest energies found for the A (electronic) and B (atomic) numbers are also drawn. A global "hull", encompassing all calculations, has a well defined transition from the A hull to the B hull at $N$~100. These hulls, similarly to the ones drawn in the theory of heterogeneous alloys, corresponds to states of total stability under the assumption of conservation in the **number** of clusters, *i.e.*, under the supposition that clusters can only change in reactions of the type

$$c(N_1) + c(N_2) \rightarrow c(N_3) + c(N_4) ,$$

where

$$N_1 + N_2 = N_3 + N_4 ,$$

and not other type of fusion or fission reactions, such as

$$c(N_1) + c(N_2) \rightarrow c(N_3) ,$$

$$N_1 + N_2 = N_3 ,$$

or

$$c(N_1) \rightarrow c(N_2) + c(N_3) ,$$

$$N_1 = N_2 + N_3 .$$

The clusters on the global hull are, in any case, very stable clusters over an extended local range.

There is a clear cross-over of cluster stability from electronic magic numbers at smaller cluster-sizes to the atomic magic numbers at larger cluster-sizes. The cross-over appears to occur at $N$~100. A number of key features from the numerical results presented in Tables 1 and 2.1-4 are to be noted :

(1) For very small clusters ($N < 50$) the kinetic energy $E_{kin}$ plays a very important role in favoring stability at the electronic rather than atomic magic numbers in their vicinity. Closed electronic shells always yield lower kinetic energy per atom than open ones.

(2) A complete outer atomic shell structure always lowers the electrostatic part of the energy. For this reason, even for cluster-sizes $N < 100$ -- dominated by the electronic magic numbers -- clusters with atomic magic numbers close to one with an electronic magic number have large binding energies. The most unstable clusters are the ones with near half-filled *d*, *f* or *g* shells of electrons. This clearly shows that even though atomic positions are extremely important for any cluster-size, the stability for smaller cluster-sizes is completely dominated by the closing of the electronic shells.

(3) For sizes $N > 100$ the most stable clusters are clearly not those corresponding to the electronic magic numbers. Although it is hard to detect any underlying pattern of atomic shell closings in this region, the most stable clusters are always found to belong to one of the three *fcc* structures built according to schemes (A2-4). Since an *fcc* lattice has a maximum possible coordination number of 12 (close-packed

structure) compared with only 8 for a *bcc* lattice, the greater stability of *fcc* clusters seems to lead credence to a spherically closed-packed arrangement as observed experimentally for clusters of somewhat larger sizes.

(4) For $N<100$, the binding energy per atom for the electronic magic numbers increases, in general, with increasing cluster-size. For the $N>100$ region the situation is more complicated as supershell structures might come into play[3,15].

(5) In the region where electronic magic numbers dominate ($N<100$) the lattice always relaxes inward, so that the effective inter-atomic distances are smaller than the corresponding value for the bulk. This fact is in agreement with the experimentally observed lattice shrinkage[23] for small clusters. As the cluster-size increases, the inward lattice relaxation becomes gradually smaller. Thus the equilibrium lattice constant increases from a value of about 96% of the bulk value for the smallest clusters to about 99% for cluster size ~200.

(6) In contrast to the results of the spherical jellium calculations, where the total energy rapidly converges to the bulk value, the present calculations clearly show that even for sizes up to ~ 200 the total electrostatic interaction energy is very different from the bulk value. The reason is that all the atoms, even in the largest cluster considered here, are only a few Ångstroms from the surface. This surface dominance is also reflected in the sizable non-uniformity in the electronic charge-density shown in Figure 1.

## IV. Conclusion

A total energy calculation based on the local pseudopotential scheme, with correlation and exchange energies taken in the local-density functional approach, yields a clear transition in the stability regime of small sodium clusters. For small number, $N<100$, clusters corresponding to closed electronic shells (**electronic** magic numbers) are considerably more stable than all others in their vicinity. For larger numbers, $N>100$, the most stable clusters are those for which the geometric configuration of the ions correspond to well defined polyhedral configurations (**atomic** magic numbers). A major effect contributing to this transition is the dominance of the electronic kinetic energy terms at low $N$, and the electrostatic contribution at large $N$. The stability of the highly coordinated *fcc* clusters appears to be a precursor to the experimentally observed stability at icosahedral or cuboctahedral packings for cluster-sizes between ~1500 and ~22,000. The reason for observing the transition at a cluster-size smaller than those observed experimentally is probably the simplification induced by the use of a simple infinite square-well potential for the electrons. This is reflected in the fact that for cluster-sizes above a hundred, the electronic charge density calculated in the present model, although it agrees well in overall features with the SJBM results[14], differs in some of the finer details. A more realistic potential, *e.g.* a finite square-well or the Woods-Saxon potential[3] used in nuclear physics, should yield a transition at larger $N$'s. Although that would involve a larger computational effort, calculations with a few hundred atoms in the scheme described here

is certainly feasible.

It should be mentioned that the cross-over effect is a consequence of a smooth relative change in the influence of the various contributions, and therefore the transition cannot be considered to be sharp. It is possible that "beats" between the two effects could be observed, with an electronic magic number becoming observable in between (and probably sufficiently removed from) consecutive atomic magic numbers. It must be finally remarked that this calculation has not attempted to determine the overall shape of the cluster of absolute minimum energy: it has simply demonstrated that geometrical structural considerations overtake electronic-shell arguments when the number of atoms in the cluster becomes larger than a typical "critical" value.

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## Appendix

This appendix gives an estimate of the error involved in the total energy calculation when one uses a spherically symmetrized charge density of electrons, by averaging over the states at the last (**partially** occupied) level. The two contributions to the total energy per atom that are going to be most affected are $E_{el\text{-}el}$ and the electrostatic part of $E_{el\text{-}ion}$ . The pseudopotential contribution $E_{ps}^{(1)}$ and the exchange-correlation energy $E_{xc}$ are themselves at least an order of magnitude smaller than either of the two electrostatic terms; corrections to these terms are negligibly small.

Let $\delta\rho(\boldsymbol{r})$ be the deviation at position $\boldsymbol{r}$ of the actual total number density of the electrons per ion from the used spherically symmetric one. Clearly,

$$\int \delta\rho(\boldsymbol{r})\, d\boldsymbol{r} = 0 \quad . \qquad \text{(A.1)}$$

Now, it is evident that the contribution to the total number density arising from all closed shells of electrons, *i.e.* due to those states *below* the Fermi level, is already spherically symmetric . Therefore $\delta\rho(\boldsymbol{r})$ arises only from those electrons on the outermost shell. Therefore $\delta\rho(\boldsymbol{r})$ can be written as the difference of the number density of the electrons at the Fermi level from the spherically symmetric electronic number density obtained by averaging over **all** states at the Fermi level. The same quantity could be equivalently written in terms of unoccupied states at the Fermi level. It is convenient to use the description in terms of either occupied or empty states, whichever number is smaller at the Fermi level. Let this number be $n$.

It should be noted that separability in the radial co-ordinate $r$ and angular variables $\Omega \equiv (\theta,\varphi)$ allows a decomposition of $\delta\rho(\mathbf{r})$ into two factors:

$$\delta\rho(\mathbf{r}) = f(r)\, g(\Omega) \quad , \qquad \text{(A.2)}$$

where $f(r) = |j_\nu(k_{\nu l}\, r)|^2$ is the same for all electrons at the Fermi level characterized by the principal and total angular momentum quantum numbers $n$ and $l$ respectively; here $j_\nu$ is the spherical Bessel's function of order $\nu$ and $k_{\nu l}$ is the $(l+1)^{th}$ zero of $j_\nu$.

Equations (A.1) and (A.2) therefore imply,

$$\int g(\Omega)\, d\Omega = 0 \quad . \qquad \text{(A.3)}$$

The correction to the electron-electron contribution $E_{el\text{-}el}$ is given by,

$$\Delta E_{el\text{-}el} = N\frac{e^2}{2}\int \frac{\{\rho_0(r)+\delta\rho(\mathbf{r})\}\{\rho_0(r')+\delta\rho(\mathbf{r}')\}}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}'$$

$$- N\frac{e^2}{2}\int \frac{\rho_0(r)\,\rho_0(r')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' \quad ,$$

$$= Ne^2\int \frac{\rho_0(r')\,\delta\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' \;+\; N\frac{e^2}{2}\int \frac{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' \quad ,$$

where $\rho_0(r)$ is the spherically symmetrized number density of electrons per ion obtained by averaging over all states at the Fermi level.

Since

$$V(r) = \int \frac{\rho_0(r')\, d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}$$

is a function of $|\mathbf{r}|=r$ only, the first term on the right hand side of the last equation becomes,

$$Ne^2 \int \delta\rho(\mathbf{r})\, V(r)\, d\mathbf{r} = Ne^2 \int f(r)V(r)r^2 dr. \int g(\Omega)\, d\Omega = 0\ ,$$

where equation (A.3) has been used. Therefore,

$$\Delta E_{el\text{-}el} = N\frac{e^2}{2} \int \frac{\delta\rho(\mathbf{r})\, \delta\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' > 0\ . \qquad \text{(A.4)}$$

Also,

$$\Delta E_{el\text{-}ion} = e^2 \sum_i \int \frac{\delta\rho(r)}{|\mathbf{r} - \mathbf{R}_i|}\, d\mathbf{r} \quad , \qquad \text{(A.5)}$$

where corrections to $E_{ps}^{(1)}$ have been neglected.

It is important to note that $\Delta E_{el\text{-}el}$ is always positive irrespective of $\delta\rho(\mathbf{r})$ . On the other hand, $\Delta E_{el\text{-}ion}$ has both positive and negative contributions. Even though (A.5) is first-order in $\delta\rho(\mathbf{r})$, whereas (A.4) second-order, it should be emphasized that (A.5) vanishes for a partially filled outer shell in jellium, whereas (A.4) does not. The term (A.4) is, in fact, responsible for the ellipsoidal distortion[24] of jellium clusters for fillings other than electronic magic numbers.

The estimation of errors can therefore be made based on (A.4), which yields, for some simple choices of $\delta\rho(\mathbf{r})$ for a few values of $l$ (>0) and small ν, and considering only non-magnetic states,

$$\Delta E_{el\text{-}el} \sim 0.1(n/N^2)E_{el\text{-}el} \quad . \qquad \text{(A.6)}$$

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**TABLE 1. ENERGY PER ATOM FOR ELECTRONIC MAGIC NUMBERS**

[ All energy components are in Rydbergs/Atom ]

| N | $E_{el\text{-}el}$ | $E_{el\text{-}ion}$ | $E_{ion\text{-}ion}$ | $E_{kin}$ | $E_{xc}$ | $E_{tot}$ |
|---|---|---|---|---|---|---|
| 8 | 1.2391 | - 2.3050 | 0.8100 | 0.1699 | - 0.2910 | - 0.3770 |
| 18 | 2.1018 | - 4.1532 | 1.7793 | 0.1650 | - 0.2950 | - 0.4021 |
| 20 | 2.2927 | - 4.5329 | 1.9677 | 0.1636 | - 0.2953 | - 0.4042 |
| 34 | 3.2017 | - 6.3382 | 2.8527 | 0.1603 | - 0.2973 | - 0.4208 |
| 40 | 3.6536 | - 7.2733 | 3.3355 | 0.1603 | - 0.2981 | - 0.4220 |
| 58 | 4.5780 | - 9.1332 | 4.2724 | 0.1569 | - 0.2988 | - 0.4247 |
| 68 | 5.1930 | -10.3257 | 4.8566 | 0.1581 | - 0.2997 | - 0.4177 |
| 90 | 6.1319 | -12.2224 | 5.8122 | 0.1552 | - 0.3001 | - 0.4232 |
| 92 | 6.2477 | -12.4628 | 5.9348 | 0.1546 | - 0.3001 | - 0.4258 |
| 106 | 6.9693 | -13.8930 | 6.6458 | 0.1556 | - 0.3009 | - 0.4232 |
| 132 | 7.9155 | -15.7607 | 7.5732 | 0.1537 | - 0.3010 | - 0.4193 |
| 138 | 8.2188 | -16.3133 | 7.8164 | 0.1532 | - 0.3011 | - 0.4260 |
| 168 | 9.2127 | -18.4019 | 8.9168 | 0.1539 | - 0.3018 | - 0.4203 |
| 186 | 9.9586 | -19.8399 | 9.6047 | 0.1524 | - 0.3018 | - 0.4260 |
| 196 | 10.4032 | -20.7524 | 10.0719 | 0.1523 | - 0.3019 | - 0.4269 |
| 198 | 10.4950 | -20.9515 | 10.1824 | 0.1524 | - 0.3020 | - 0.4237 |
| 232 | 11.4760 | -22.9042 | 11.1480 | 0.1523 | - 0.3024 | - 0.4303 |

**TABLE 2.1. ENERGY PER ATOM FOR ATOMIC MAGIC NUMBERS**
**( corresponding to finite *bcc* lattice clusters)**

[ All energy components are in Rydbergs/Atom ]

| N | $E_{el\text{-}el}$ | $E_{el\text{-}ion}$ | $E_{ion\text{-}ion}$ | $E_{kin}$ | $E_{xc}$ | $E_{tot}$ |
|---|---|---|---|---|---|---|
| 9 | 1.3347 | - 2.4834 | 0.8942 | 0.1756 | - 0.2906 | - 0.3695 |
| 15 | 1.8653 | - 3.7496 | 1.6100 | 0.1725 | - 0.2932 | - 0.3950 |
| 27 | 2.7594 | - 5.5036 | 2.4774 | 0.1662 | - 0.2956 | - 0.3962 |
| 51 | 4.2270 | - 8.5267 | 4.0327 | 0.1600 | - 0.2981 | - 0.4051 |
| 59 | 4.6407 | - 9.1784 | 4.2556 | 0.1572 | - 0.2988 | - 0.4237 |
| 65 | 5.0171 | -10.0526 | 4.7625 | 0.1582 | - 0.2992 | - 0.4140 |
| 89 | 6.0903 | -12.3516 | 5.9925 | 0.1555 | - 0.3000 | - 0.4133 |
| 113 | 7.2265 | -14.6726 | 7.1688 | 0.1561 | - 0.3007 | - 0.4219 |
| 137 | 8.1683 | -16.6656 | 8.2216 | 0.1533 | - 0.3011 | - 0.4235 |
| 169 | 9.2546 | -18.4671 | 8.9386 | 0.1539 | - 0.3018 | - 0.4218 |
| 181 | 9.7532 | -19.3720 | 9.3444 | 0.1529 | - 0.3017 | - 0.4232 |

**TABLE 2.2. ENERGY PER ATOM FOR ATOMIC MAGIC NUMBERS**
**( corresponding to finite *Type-I fcc* lattice clusters)**

[ All energy components are in Rydbergs/Atom ]

| N | $E_{el-el}$ | $E_{el-ion}$ | $E_{ion-ion}$ | $E_{kin}$ | $E_{xc}$ | $E_{tot}$ |
|---|---|---|---|---|---|---|
| 13 | 1.6896 | - 3.2914 | 1.3263 | 0.1766 | - 0.2920 | - 0.3909 |
| 19 | 2.1970 | - 4.3470 | 1.8778 | 0.1644 | - 0.2947 | - 0.4025 |
| 43 | 3.8117 | - 7.5802 | 3.4905 | 0.1611 | - 0.2979 | - 0.4148 |
| 55 | 4.4281 | - 8.8099 | 4.1072 | 0.1584 | - 0.2985 | - 0.4147 |
| 79 | 5.6673 | -11.2833 | 5.3438 | 0.1577 | - 0.2996 | - 0.4141 |
| 87 | 6.0062 | -11.9582 | 5.6743 | 0.1560 | - 0.2999 | - 0.4216 |
| 135 | 8.0670 | -16.0499 | 7.7075 | 0.1535 | - 0.3010 | - 0.4229 |
| 141 | 8.3192 | -16.6369 | 8.0351 | 0.1536 | - 0.3011 | - 0.4301 |
| 177 | 9.5880 | -19.0662 | 9.1990 | 0.1533 | - 0.3017 | - 0.4276 |
| 201 | 10.5821 | -21.1489 | 10.2932 | 0.1525 | - 0.3020 | - 0.4231 |

**TABLE 2.3. ENERGY PER ATOM FOR ATOMIC MAGIC NUMBERS**
**( corresponding to finite *Type-II fcc* lattice clusters)**

[ All energy components are in Rydbergs/Atom ]

| N | $E_{el-el}$ | $E_{el-ion}$ | $E_{ion-ion}$ | $E_{kin}$ | $E_{xc}$ | $E_{tot}$ |
|---|---|---|---|---|---|---|
| 16 | 1.9409 | - 3.8357 | 1.6303 | 0.1700 | - 0.2938 | - 0.3883 |
| 28 | 2.8240 | - 5.6009 | 2.5076 | 0.1656 | - 0.2958 | - 0.3995 |
| 44 | 3.8641 | - 7.6843 | 3.5448 | 0.1612 | - 0.2978 | - 0.4120 |
| 68 | 5.1930 | -10.3257 | 4.8566 | 0.1581 | - 0.2997 | - 0.4177 |
| 80 | 5.7100 | -11.2459 | 5.2609 | 0.1576 | - 0.2996 | - 0.4170 |
| 104 | 6.8678 | -13.6798 | 6.5375 | 0.1561 | - 0.3007 | - 0.4191 |
| 140 | 8.2857 | -16.5144 | 7.9477 | 0.1535 | - 0.3011 | - 0.4286 |
| 152 | 8.6857 | -17.3414 | 8.3773 | 0.1543 | - 0.3013 | - 0.4254 |
| 180 | 9.7120 | -19.3947 | 9.4122 | 0.1530 | - 0.3017 | - 0.4192 |

**TABLE 2.4. ENERGY PER ATOM FOR ATOMIC MAGIC NUMBERS**
**( corresponding to finite *Type-III fcc* lattice clusters)**

[ All energy components are in Rydbergs/Atom ]

| N | $E_{el\text{-}el}$ | $E_{el\text{-}ion}$ | $E_{ion\text{-}ion}$ | $E_{kin}$ | $E_{xc}$ | $E_{tot}$ |
|---|---|---|---|---|---|---|
| 14 | 1.7748 | - 3.4752 | 1.4315 | 0.1747 | - 0.2926 | - 0.3868 |
| 38 | 3.5040 | - 7.0220 | 3.2353 | 0.1607 | - 0.2974 | - 0.4194 |
| 68 | 5.1930 | -10.3257 | 4.8566 | 0.1581 | - 0.2997 | - 0.4177 |
| 92 | 6.2477 | -12.4628 | 5.9348 | 0.1546 | - 0.3001 | - 0.4258 |
| 116 | 7.3363 | -14.6532 | 7.0340 | 0.1559 | - 0.3007 | - 0.4277 |
| 164 | 9.0816 | -18.0950 | 8.7420 | 0.1541 | - 0.3017 | - 0.4190 |
| 188 | 10.0476 | -20.0052 | 9.6792 | 0.1524 | - 0.3018 | - 0.4278 |
| 236 | 11.6235 | -23.2000 | 11.2918 | 0.1522 | - 0.3023 | - 0.4348 |

## Figure captions

Figure 1.

The electronic number density in the model under consideration for various electronic magic numbers as a function of the radial distance from the center of the spherical cluster. The number density is in units of the corresponding jellium density $\rho_0$, shown by the dashed line. The radial distance is in units of the total radius $R$ of the electron confining sphere (infinite potential well). (a) N = 8; (b) N = 34; (c) N = 58; (d) N = 92; and (e) N = 168.

Figure 2.

Plot of the total energy per atom as a function of cluster-size $N$ for various electronic and atomic magic numbers (Tables 1 and 2). The **crosses** represent the points corresponding to the **electronic** magic numbers and the **squares** correspond to the **atomic** magic numbers. The "hulls" of minimum energy are drawn separately for the electronic and the atomic magic numbers, with a line joining them to form the overall minimum-energy hull. A clear transition is observed between $N = 58$ (electronic magic number) and $N = 141$ (atomic magic number).

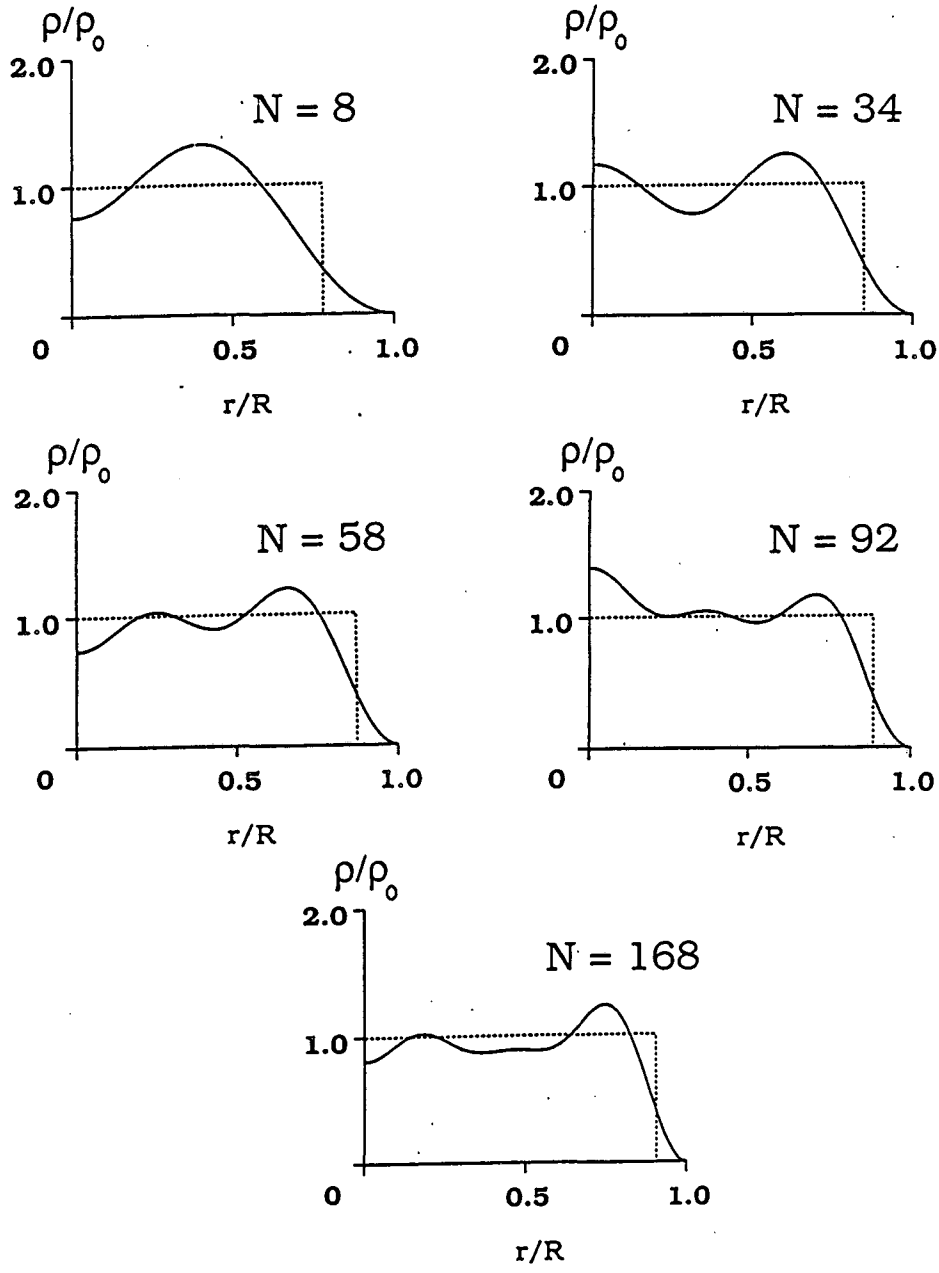


Figure 1

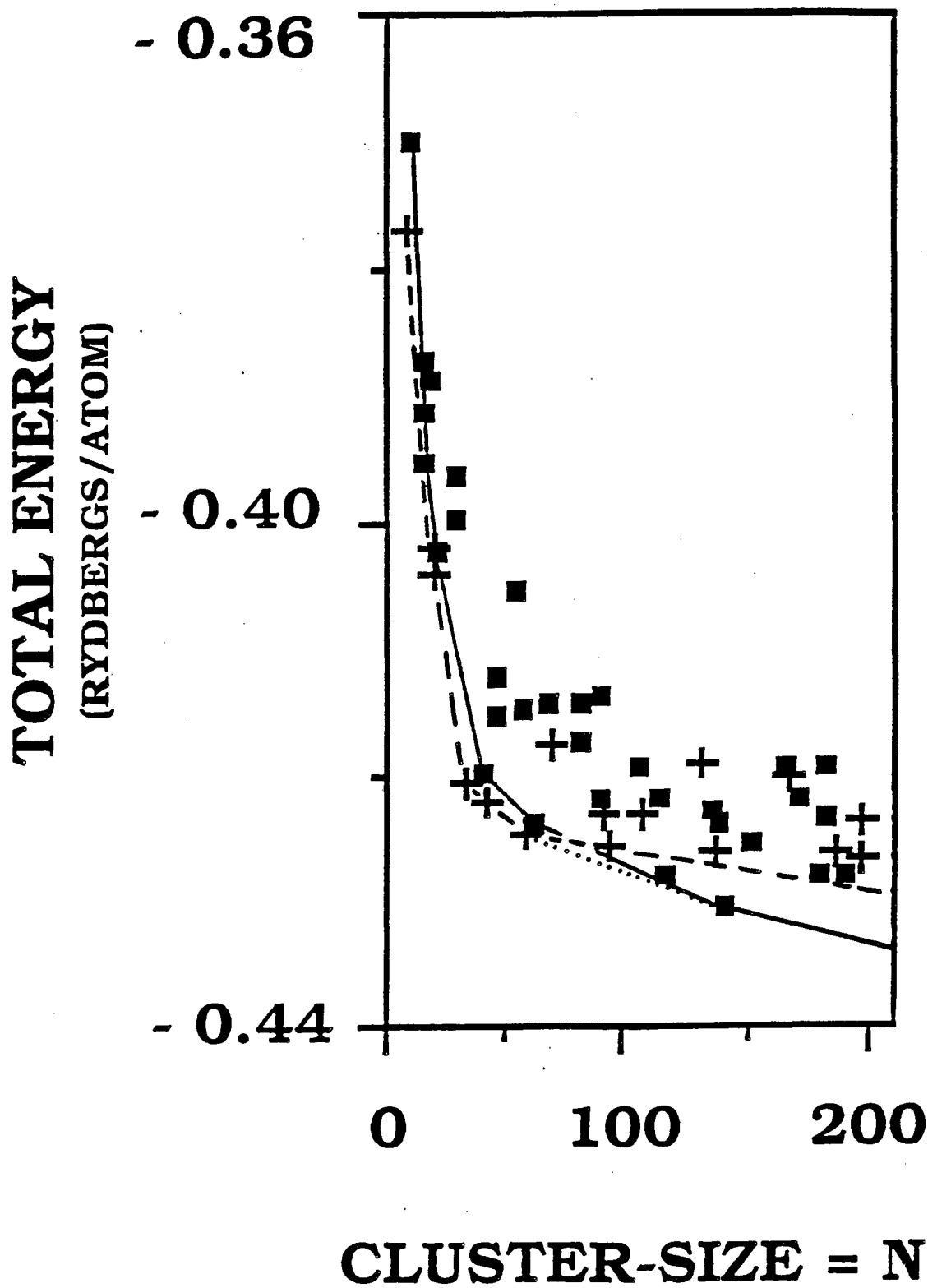
- 0.36
- 0.40
- 0.44
TOTAL ENERGY
(RYDBERGS/ATOM)
0
100
200
CLUSTER-SIZE = N

Figure 2

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