

THE PHYSICS OF METAL CLUSTERS

Theorists and experimenters find that small aggregates of metal atoms exhibit a shell structure like that of atomic nuclei. With this knowledge they hope to determine which properties define 'metallic' over the range from atom to bulk.

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Scientists often set the stage for their most productive advances by first developing simple models, even when sophisticated first-principles tools are available. These models usually originate from the necessity to explain experimental observations. If the models are robust, then a variety of data fall into place, and successful predictions are made. If a model is "correct," it is eventually found to be consistent with or derivable from fundamental theory. The Bohr model for atoms is a prime example. Ernest Rutherford's experiments showed that J. J. Thomson's "plum pudding" model of an atom, consisting of a positive spherical "pudding" embedded with negative electron "plums," had to be replaced by Rutherford's nuclear picture, and subsequent optical data led to the Bohr model. Eventually quantum theory confirmed that the Bohr model is an excellent rudimentary representation for an atom. Although it has been superseded by more elaborate quantum theoretical approaches, this model is still taught to students of atomic physics because of the physical insight one gains by using the Bohr picture of an atom.

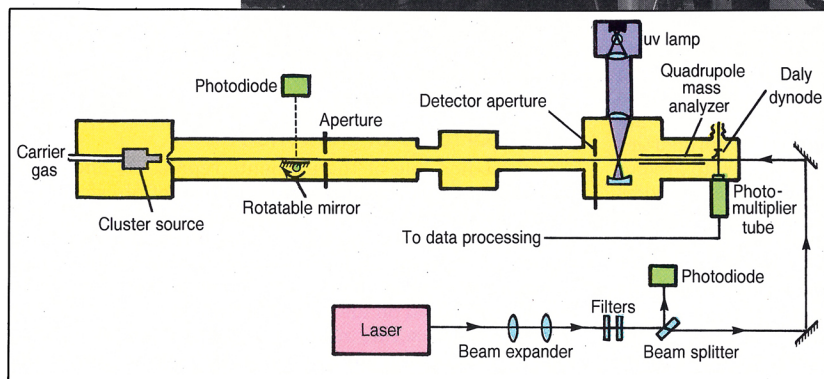
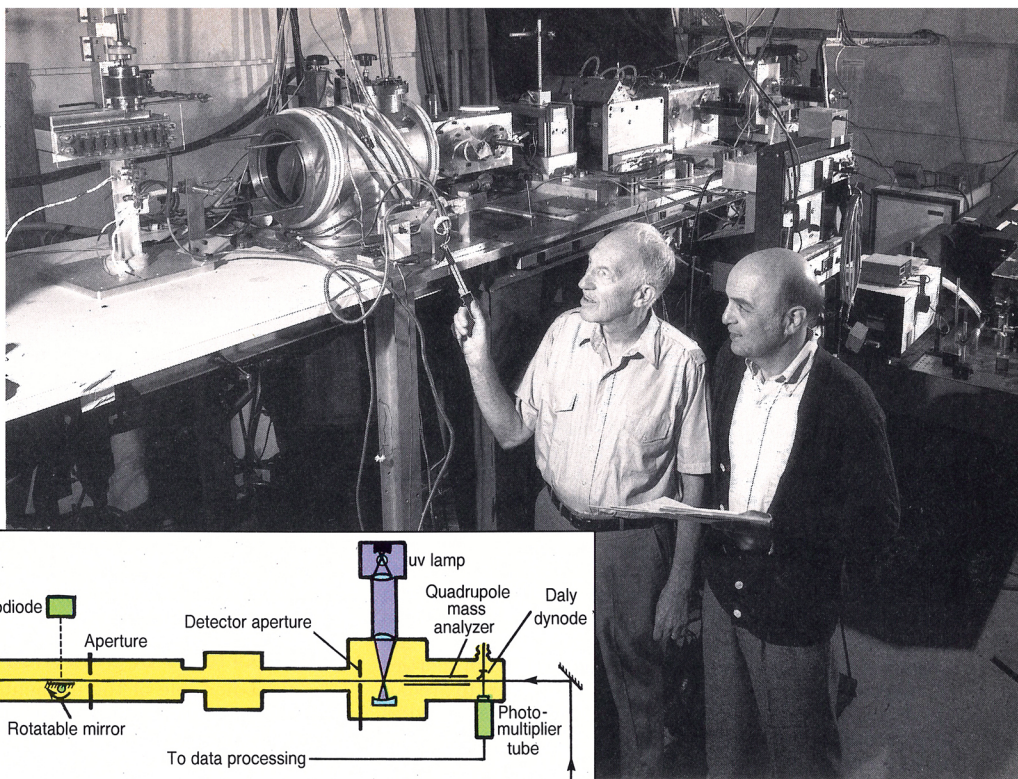
It is appealing to make parallel arguments for the Thomson-like model currently being used for metallic clusters,¹ where electron waves replace the electrons, and a positive jelly or "jellium" replaces the pudding. This model provides an accurate description of some simple metal clusters and has the potential to be robust in the sense discussed above. Within certain limits, the model can be justified from first-principles quantum theory. The jellium model treats metal clusters as "giant atoms" with electron energy levels that exhibit "shell structure." The shell structure² is similar to that found for nuclei, and as a result, cluster physics has benefited greatly from analogies with nuclear physics.

Between atom and crystal

The terms "cluster" and "microcluster" are usually used to describe aggregates of atoms that are too large to be referred to as molecules and too small to resemble small pieces of crystals. These aggregates generally do not have the same structure or atomic arrangement as a bulk solid and can change structure with the addition of just one or a few atoms. As the number of atoms increases, eventually a crystal-like structure is established, and the addition of new atoms doesn't change the bulk structure. Surface rearrangements may still take place on crystals with adatoms, but these are usually less drastic than the changes that occur when atoms are added to smaller clusters.

Not all clusters can be described by the jellium model. The properties of the atoms making up the cluster dictate many cluster properties. Consider the following second-

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Supersonic cluster-beam apparatus at University of California, Berkeley, produces alkali metal clusters of 2 to 100 atoms (a). Experimenter Walter Knight points out the source chamber to theorist Marvin Cohen. A schematic of the cluster-beam apparatus for measuring photoabsorption cross sections of sodium clusters (b) shows its many components. A laser beam propagates in a direction opposite that of the cluster beam, which is thus heated by the absorption of photons. A neutral atom is evaporated and the recoiling daughter cluster is removed from the beam. The wavelength dependence of the beam depletion gives absolute values of the absorption cross section. For the spherical Na_8 cluster the cross section shows a surface plasma resonance at 480 nm. One selects the desired interaction region in this experiment by pulsing the beam and gating the detector. **Figure 1**

row atoms of the periodic table: Ne, Na, Mg, Al and Si. Since Ne is a closed-shell atom, its interatomic interactions are weak and isotropic. Clusters of Ne and other rare gases are therefore composed of atoms that behave like billiard balls, and aggregates are expected to have icosahedral structures. In contrast, Na prefers metallic bonds formed by itinerant electrons. Just as the jellium model for solid Na is an appropriate starting point for describing its solid-state properties, the jellium sphere is a good starting point for examining clusters of Na. In this model, the positive ion cores are "smeared out" into a positive background, and the nearly free electrons are considered to respond quantum mechanically to the positive potential. Hence the electrons are mostly confined to the jellium sphere with some "spill-out" at the edges.

Let us skip over Mg and Al for a moment and consider Si. Because Si tends to form covalent bonds, it is not expected that all the valence electrons in a Si cluster will either localize close to the atom, as in Ne, or become completely itinerant, as in Na. For this case a more appropriate picture may be a Newton atom—a particle with "hooks" that enable it to couple with other atoms. Thus Si tends to form clusters that can be represented by

ball-and-stick structural models: Here the balls are the Si cores, and the sticks are the covalent bonds formed from the valence electrons. Returning to Mg and Al, we find that clusters of these atoms behave in a manner somewhere between Na and Si: In large clusters, the itinerant nature of the electrons is evident, and a jellium approximation is appropriate. In small clusters some directional bonding is expected and structural effects become more important.

Trend toward miniaturization

Part of the motivation for studying clusters is the desire to understand how physical properties evolve in the transition from atom to molecule to cluster to small particle to bulk solid. Another motivation is associated with questions arising from the desire to use smaller and smaller solid structures in technological applications. Miniaturization in electronics is a prime example of this trend, and advances in this area indicate that confinement, as achieved in quantum dots (which are essentially clusters deposited on a surface), is leading to effects similar to those seen in clusters. Research on catalysis and on related areas that exploit the high surface-to-volume ratios of

small particles and clusters also requires information about small systems. This connection explains the strong links between researchers studying the surfaces of solids and those studying small particles and clusters.

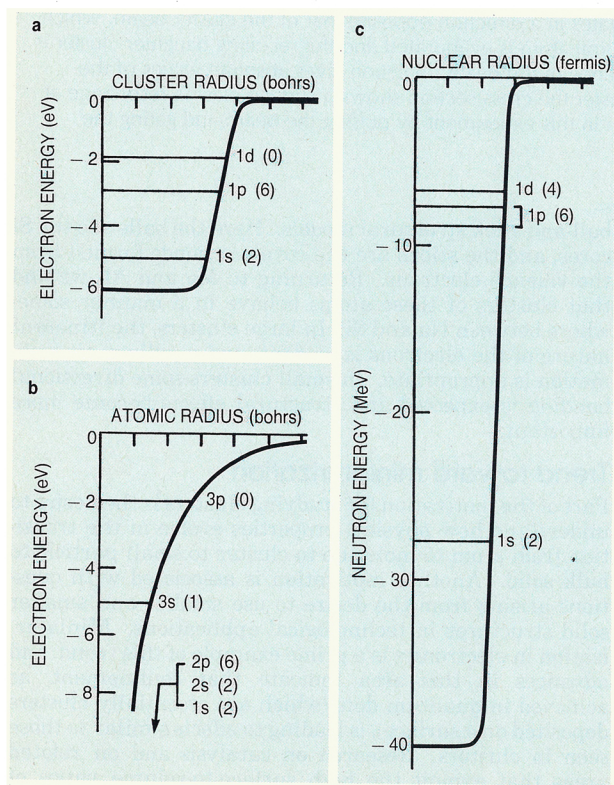
Because of the variety of fields in which interest in clusters has arisen, approaches to their study vary considerably. Some quantum chemists and physicists have tended to consider the evolution of clusters from atoms and molecules, and many useful calculations have been done that begin with electronic structural approaches designed originally for computing the properties of molecules. Total-energy calculations are used to predict structural arrangements for small clusters; these studies are particularly useful for nonmetallic clusters such as those containing C and Si. Here, in contrast, we focus on the jellium model, which is based on a condensed matter physics approach for bulk metals. The jellium model was first verified in a study of abundance spectra of Na clusters.³ The model explained why certain cluster sizes are more stable and dominate the experimentally observed spectra. (Figure 1 shows an instrument used both to generate and study clusters.) The numbers of atoms in these favored clusters were referred to as "magic

numbers," and these numbers were shown to be a direct consequence of the electronic shell structure of the clusters. Hence, for free-electron-like metallic clusters, it is the energy of the itinerant electrons that dominates in determining the clusters' stability. In this picture, the energy associated with the positions of the atomic cores determines the internal structure of the cluster, but this structural energy accounts for only a perturbation on the overall electronic energy.

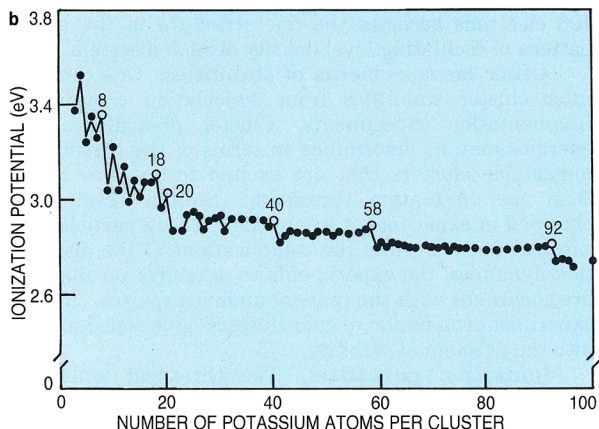
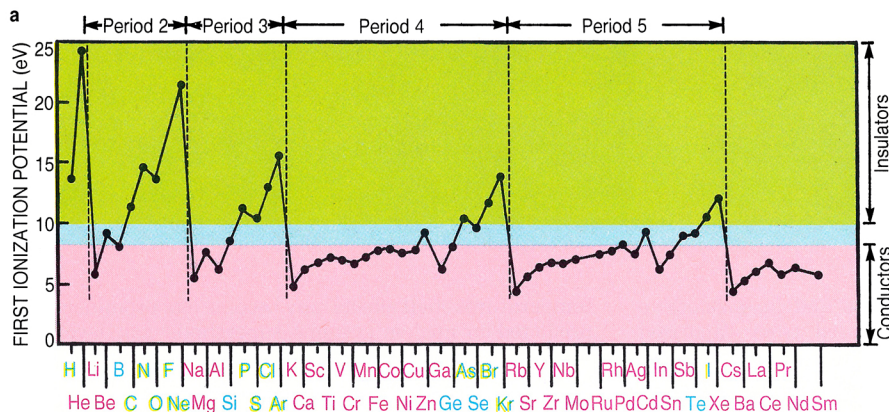
Historical roots of shell models

The periodic table of the elements represents one of the first successes in organizing a large body of physical facts about atoms that have homologous structures. The development of the periodic table ultimately led to a theory of valency and stimulated the development of inorganic chemistry. In its early development, the periodic table was based on ideas such as "the law of octaves," by which certain serial numbers identify members of a sequence as having similar properties—for example, the rare gases. Later, the periodic table was organized according to successive electron shells. Our understanding of the ultimate limit to the size of the atoms themselves had to wait for the shell model of nuclear physics, in which "magic numbers" signify unusual stability and abundance for certain nuclei—analogous to the high stabilities for the rare gases in the atomic sequence. The energy-level diagrams in figure 2 illustrate the analogies between nuclear, atomic and cluster shell structures.

The electronic shell model of simple metal clusters correctly produces the observed electronic properties as a function of the number of free electrons in a cluster. It is this size dependence of properties that atoms, nuclei and clusters have in common. While the electronic structure of atoms depends on the central Coulomb potential, the



Potential wells and energy levels for three fermion systems: a sodium metal cluster containing eight atoms (a), a sodium atom (b) and a sodium nucleus (c). Na₈ is a closed-shell cluster system and has a high excitation energy and relatively high ionization potential. In the periodic table the sodium atom follows neon, which has a closed shell and a relatively low binding energy. The Na²³ nucleus, which has 11 protons and 12 neutrons, lies in the open-shell region between nuclear magic numbers 8 and 20. The binding energy for the cluster electron is approximately 3 eV, and that for a nucleon, approximately 8 MeV. Properties of clusters and nuclei are described in terms of relatively flat potential wells characteristic of the mean-field approximation. The numbers in parentheses indicate the occupancies of the levels. A bohr is equal to 0.5292 Å. **Figure 2**



Shell structure: Two views. **a:** Atomic ionization potentials drop abruptly from above 10 eV following the shell closings for the noble gases (He, Ne, Ar and so on). For semiconductors (labeled in blue) the ionization potential is between 8 and 10 eV, while for conductors (red) it is less than 8 eV. It is clear that bulk properties follow from the natures of the corresponding atoms. (Adapted from A. Holden, *The Nature of Solids*, © Columbia U. P., New York, 1965. Reprinted by permission.) **b:** Ionization potentials for clusters of 3 to 100 potassium atoms show behavior analogous to that seen for atoms. The cluster ionization potential drops abruptly following spherical shell closings at $N = 8, 20, 40, \dots$. Features at $N = 26$ and 30 represent spheroidal subshell closings. The work function for bulk potassium metal is 2.4 eV. **Figure 3**

more uniform harmonic oscillator or Woods-Saxon potential proves more suitable for describing symmetries of nuclei.

The use of parallel methods and models in atomic, nuclear and condensed matter physics has yielded mutual benefits for many years. For example, the resonance methods for studying nuclear moments provided crucial data needed to fill out the picture of the nuclear shell model. In turn, the nuclear moments are used as noninvasive probes for the analysis of microscopic fields in molecules, liquids and solids. Similarly, the ideas of pairing theory and the models of superconductivity have stimulated advances in both nuclear and condensed matter physics. The study of single-particle and collective dynamics in atomic, nuclear and cluster systems enlarges our knowledge of all of these systems.

What makes metal clusters 'metallic'?

Clusters may be classified as metallic or nonmetallic according to the atoms they are made of, and we shall see that in general some metallic character persists from small clusters to bulk matter of the same composition. Although a large effort in cluster science has been devoted to studying nonmetal and molecular clusters, we will not consider this area in detail here. Attempts to discover metal-insulator transitions have, in most cases, not been successful.

The fundamental question that arises then is, What is the metallic character that persists through a sequence of clusters and emerges in the bulk material? It seems likely that clues are to be found in the atomic wavefunctions, and pursuit of the answers to this question should lead to further definition of what is meant by "metallic." Figure 3a shows that atoms are easily classified as metallic,

nonmetallic or semiconducting purely in terms of their ionization potentials. Similar behavior is observed in clusters when the ionization potentials are measured as a function of the number of atoms in a cluster (figure 3b).

Metal clusters can be prepared in the laboratory by condensing metal vapor as it expands through a nozzle in the cluster source. There are obvious advantages to collecting significant quantities of preserved cluster material in a glass or rare-gas matrix for experimental or commercial purposes. However, in the present state of the art, the possibilities for collecting significant amounts of clusters that all contain the same number of atoms are limited. Aside from the difficulties of preparing such materials, there is a fundamental problem arising from cluster-matrix interactions. These interactions will be difficult to determine without prior knowledge of the noninteracting free clusters.

The production and study of isolated, noninteracting clusters has been a high priority among cluster scientists, and these studies are proceeding in parallel with efforts to produce and store quantities of matrix-preserved systems. However, the price of purity is scarcity, because the concentration of clusters in beams is miniscule compared with what one desires for most practical uses. Our hope for the future is to produce large quantities of identical deposited clusters whose properties in the pure state are known.

Cluster-beam machines

Typical contemporary cluster-beam machines have designs based on patterns developed years ago in the classic atomic- and molecular-beam experiments. Figure 1 shows the experimental apparatus at Berkeley. The principal components are the cluster source, supersonic nozzle,

collimating slits, interaction regions and mass-selective detector. The clusters are condensed from vaporized metal during cooling in the supersonic nozzle, through which the clusters are carried by a jet of inert gas at high pressure. Vaporization is accomplished by direct heating or by exposing a piece of metal to intense laser radiation. The collimating slits define a path that, if followed by the beam, leads to detection. The interaction regions may contain one or several of the following: static electric or magnetic fields; scattering agents such as electrons, neutral or ionized atoms, molecules or clusters; chemical reagents; or electromagnetic radiation ranging from microwaves or ir to uv. The degree of deflection of the cluster beam by applied electric or magnetic fields in the interaction region is a measure of the interaction strength.

Experimental data are available for a number of metal clusters, containing up to 10 000 atoms in some cases. These results include mass abundance, fragmentation, photoelectron and plasma resonance spectra as well as binding energies, ionization potentials, electron affinities, static electric polarizabilities, ferromagnetic moments and chemical reactivities. Study of neutral metal clusters and their positive and negative ions shows that their behavior depends primarily on the number N of delocalized electrons. However, this simple picture needs to be modified when it is applied to polyvalent and transition metals. This modification represents one of the principal challenges in extending our range of understanding of the cluster systems. Some experimental results are discussed in detail below.

Measurements on metallic clusters

Stabilities and magic numbers. The most conspicuous features in the mass abundance spectra represent "spherical" shell closings, which occur when electronic levels are completely filled and produce electronically spherical clusters. "Spheroidal" deformations of clusters, which occur when some subshells are partially filled, also produce recognizable features.⁴ Experimental mass abundance spectra (such as that in figure 4a) are, in general, good indicators of relative binding energies and other electronic properties, but the spectra can be distorted by the effects of apparatus characteristics such as nozzle shapes and temperatures. A cold nozzle, however, can minimize excitations so that the data reflect primarily ground-state behavior. Recently developed sources⁵ exploit a sequence of separate processes—metal vapor generation, cluster growth and cooling during nozzle expansion—to make cold clusters. The mass spectra thus produced may not exhibit the quasiequilibrium abundances obtained when these processes are more or less simultaneous. Nevertheless, examination of the clusters made with these sources reveals the same electronic properties one sees for individual mass-selected clusters. Similarly, a liquid metal ion source often gives different sets of mass abundance numbers because thermal equilibrium is not established during cluster formation. At high

temperatures shell effects may become less prominent. As predicted for nuclear systems, supershells⁶ can develop in large clusters as N approaches 1000. The supershells result from a level-bunching effect involving interference between amplitudes in classical orbits. The shell structure associated with energy gaps in a system with roughly 100 electrons becomes the fine structure in the larger pattern of oscillating level density of such a system.

Other measurements of stabilities. One can also infer cluster stabilities from dissociation energies in fragmentation experiments. Cluster photodissociation energies may be determined in terms of the lifetimes of metastable clusters that are excited to energies larger than the dissociation threshold.⁷ Similar results are obtained in experiments where the exciting particles are rare-gas ions. Despite the complications of the dissociation dynamics, the experiments to date give results that are consistent with the mass abundance spectra. Recent experiments on fission of gold clusters⁸ give added insight into the problem of stability.

Ionization potentials. The threshold ionization potentials for sequences of alkali metal clusters^{1,5} drop abruptly following spherical and ellipsoidal shell closings (see figure 3b). In the early days of cluster investigations, one worried whether dissociation occurring with ionization would distort the mass spectra, but that worry has proven unfounded, providing the clusters are not too hot and the ionizing radiation is not too intense. The breadth of the ionization threshold depends on the cluster temperature. In general, it is found that shell effects are superposed on an $N^{-1/3}$ cluster-size dependence, a trend that is believed to stem from electrostatic charging effects. The good correlation between mass abundance spectra and the corresponding ionization potentials initially served to support the idea that observed shell effects are electronic in origin and that the jellium model was applicable to simple metal clusters. Recent measurements on Al clusters suggest the existence of a more complicated electronic structure for such systems.⁹

Photoelectron spectroscopy. Photoelectron spectra of clusters give the electron affinities and energy levels. This is a genuine spectroscopy of the electronic levels of the systems, and the results are in good agreement with other level spectroscopies that identify shell closings. The observation of the evolution of the d band in a long sequence of Cu clusters¹⁰ (figure 5) represents a major step in studying the evolution from cluster to bulk metallic electronic structure. In fact, indications of bulk metallic properties are recognizable in even the smallest clusters, and the transition to bulk-like behavior takes place gradually.

Static electric polarizability. This property is a direct measure of electronic screening. Early predictions of reduced screening and metal-insulator transitions in small clusters were not borne out in experiments. The pervasive jellium implies delocalization of the conduction electrons and suggests the onset of metallic behavior with the smallest cluster. Because the shell model implies that

Abundance spectrum measured for Na clusters (a) compares favorably with the calculated second-order energy difference between neighboring clusters in a sequence (b). The measured data show stable cluster sizes at the magic numbers, which correspond to closed electronic shells. The calculated spectrum reproduces the peaks because of the special stability of clusters with closed shells. The second-order energy difference is used to remove any reference to the energy of isolated atoms. **Figure 4**

there is a large energy gap in the excitation spectrum above shell closings, one expects spherical clusters to have low polarizabilities compared with adjacent clusters in a sequence. This is indeed what is observed.⁴

Plasma resonance frequencies. Plasma resonances in clusters are analogous to giant dipole resonances in nuclei. Using the plasmon pole approximation, we can predict plasma resonance frequencies^{11,12} from the dynamic polarizability, which is derivable from the static polarizability. The peak photoabsorption wavelengths can in fact be used to determine the polarizability tensor. Beam depletion experiments give absolute photoabsorption cross sections directly.¹² These measurements provide some insight into the dynamics of absorption, thermalization and evaporative fragmentation, which occur in beam depletion experiments. Enough experimental data are now available to stimulate further theoretical studies of the related relaxation mechanisms.

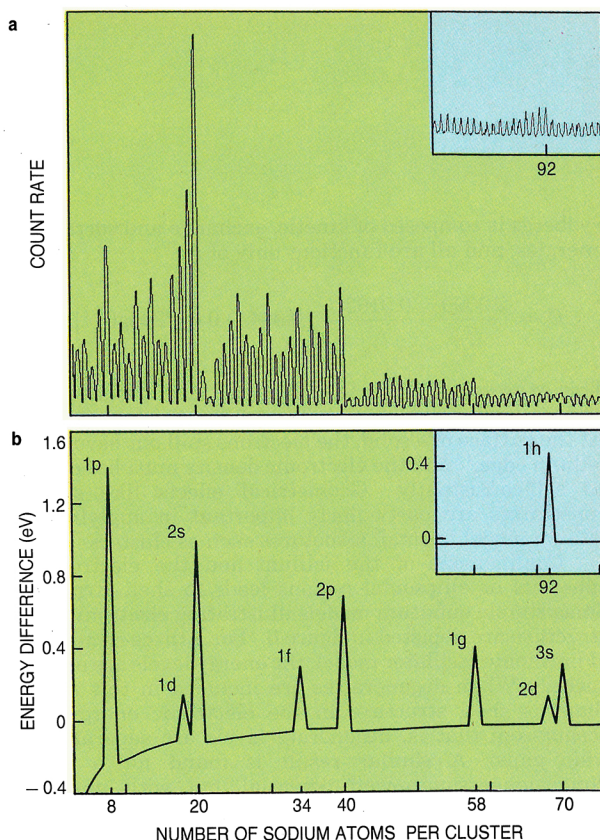
The photoabsorption data for a series of sodium clusters provide information concerning the shell structure of clusters and show the transitions from single-particle behavior to the collective motion of Na clusters with N equal to 3, 4 or 5; to oblate structures for N equal to 6 or 7; to spherical structure for N equal to 8; to prolate structures for N of 9 or 10; and ellipsoidal behavior for N equal to 11 or 12. For clusters with more than 12 electrons, there is evidence of peak fragmentation. Missing oscillator strengths in the plasma resonance curves imply the existence of yet unobserved absorption peaks.¹³ Plasma peak widths reflect interactions associated with zero-point and thermal shape oscillations¹⁴ of the clusters. It is interesting that the damping of plasmon resonances appears to be related to the origins of electrical resistance.

Collective behavior in CsO clusters suggests metallic behavior,¹⁵ which can also be expected in other materials not ordinarily thought to be metallic. Again we see the need for a more comprehensive definition of "metallic."

Magnetic moments. Early Stern-Gerlach experiments on the Na trimer¹ were expected to show a beam deflection similar to that of an atom with three times sodium's mass. However, spin-rotation coupling and hyperfine structure greatly complicated the deflection patterns. These results indicated that larger clusters are unlikely to show resolved Stern-Gerlach peaks. Recent results on iron clusters of up to 500 atoms¹⁶ show one-sided deflections indicating intracluster spin relaxation. Temperature-dependent moments are observed to increase with N . The moments are about 1 Bohr magneton, which is less than the value for bulk Fe. Further experiments on the magnetic field, temperature and size dependences of Fe clusters are expected to contribute significantly to our knowledge of ferromagnetic behavior.

Chemical reactions. Chemical reactivity reflects relative cluster stability. One can, for example, probe stability by studying the formation of CsO clusters,¹⁵ which exhibit metallic shell effects as well as plasmon resonances.

In general, the experimental data either confirm or



elaborate the idea of electronic shell structure in clusters and indicate directions for further development. The contrast between the rather good agreement with the jellium-based shell model for the monovalent metals and the disagreements⁵ seen for Al points the way toward further refinements of the theoretical models.

The jellium model

The jellium model for bulk solids is a simplified type of one-electron model in which an electron is assumed to interact with the average potential generated by the other electrons and the ions. In the one-electron model, the total electronic Hamiltonian is the sum of the energies of the individual electron Hamiltonians. This is a great simplification. When a pseudopotential is used to describe the ion-electron interaction, and the electron-electron interaction is calculated using a local-density approximation, it is relatively straightforward to calculate the total electronic energy for a known structural arrangement of atoms. This approach has been applied to a variety of solids¹⁷ and to structural models of metal clusters.

The transition from a pseudopotential model to a jellium model requires the smearing out of the background of positive ions. The solid is then structureless, and the positive background charge density $+e\rho_0$ is canceled by an electronic contribution $-e\rho_0$, fixing the charge neutrality. The system is characterized by the electron-gas parameter r_s , which is the radius of the volume per electron measured in units of the Bohr radius a_0 . Hence

$$\frac{4}{3}\pi(r_s a_0)^3 = \frac{1}{\rho_0} = \frac{\Omega}{N} \quad (1)$$

Here N is the total number of electrons and Ω is the volume of the solid. The total electronic energy E_e in

rydbergs is composed of kinetic, exchange and correlation energies, and all are functions only of r_s :

$$E_e = \frac{2.2099}{r_s^2} - \frac{0.9163}{r_s} - [0.094 - 0.0622 \log(r_s)] \quad (2)$$

This expression for E_e is accurate as r_s approaches zero and for large solids, for which surfaces can be neglected. At the surface of a solid, the electrons spill out beyond the jellium edge,¹⁸ and the electronic density must be computed self-consistently. Geometrical effects like surface constraints are particularly important in applying the jellium model to small structures such as clusters.

Confinement of the jellium and the electrons to spherical or ellipsoidal regions leads to shell structure. Some simple quantum models illustrating electronic shell structure are depicted in figure 6. For a three-dimensional harmonic oscillator model, the energy levels are equally spaced. When degeneracies are included in this model, there is shell structure in the electronic energy-level occupation; that is, degenerate levels are separated by wide gaps. A similar result is found for a three-dimensional square-well potential, but with unevenly spaced energy levels. A model that gives results similar to those found in self-consistent jellium calculations is intermediate between the harmonic oscillator and square-well models. In this model the energy levels are characterized by principal and angular momentum quantum numbers (n, l). However, unlike in the model for atoms (figure 2), where l must be less than n , in this case there is no restriction on the relative values of l and n because the potential is not of the Coulomb form. The successive energy levels (and their degeneracies) for the intermediate model are 1s (2), 1p (6), 1d (10), 2s (2), 1f (14), 2p (6), 1g (18), 2d (10), 3s (2), 1h (22), 2f (14), 3p (6), 1i (26), 2g (18).... Hence, as electrons fill the shells, closings occur for total electron numbers 2, 8, 18, 20, 34, 40, 58, 68, 70, 92, 106, 112, 138, 156 and so on. In clusters of alkali or noble metals each atom contributes one electron, and shell closures occur for clusters containing the numbers of atoms in this series. Total energies should be low for clusters having these "magic numbers," and hence clusters of these sizes are expected to be particularly stable.

As discussed earlier, the abundance spectra for metal clusters show that clusters that have magic numbers of atoms are indeed copious. Although a number of *ab initio* studies have been performed for clusters with approaches such as the pseudopotential method, self-consistent-field molecular-orbital methods, the Hückel molecular-orbital method and the generalized-valence-bond formalism, these calculations have usually been limited to small clusters. If one needs an estimate of the total energy, then one does energy minimizations for competing cluster geometries. As the number of atoms in a cluster increases, this calculation becomes increasingly difficult. There is no size limitation on the spherical jellium calculation because no optimization of crystal structure is needed. Each atomic species is characterized by a different r_s , and a self-consistent calculation is performed for each N . For nonspherical jellium, finding the optimum shape can involve several iterations.

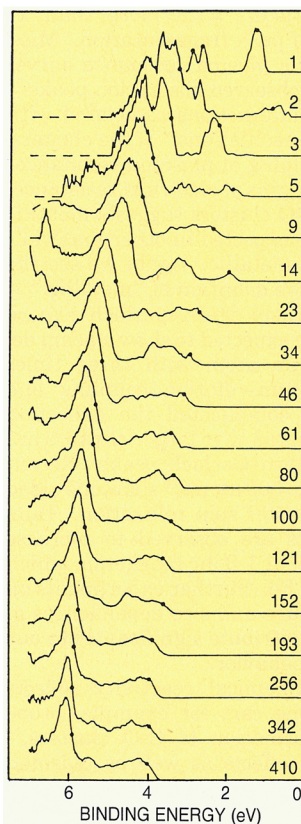
The jellium calculation of the total energy yields dips at the magic numbers. To make comparisons with the measured abundance spectra, it is useful to calculate the second derivative of the total energy with respect to N ,

$$\Delta_2(N) \equiv 2E(N) - E(N-1) - E(N+1) \quad (3)$$

where $E(N)$ represents the total energy for an N -atom cluster. It can be argued that if the clusters in the nozzle region are approximately in local thermal equilibrium, then the density distribution of clusters is unchanged during the free expansion and ionization process, and the observed abundances at temperature T can be expressed as

$$\log \frac{I_N^2}{I_{N-1} I_{N+1}} \propto \frac{\Delta_2(N)}{kT} \quad (4)$$

where I_N is the abundance intensity for an N -atom cluster and k is Boltzmann's constant. Figure 4b shows a comparison between the experimental abundance spectrum and $\Delta_2(N)$ for Na clusters. The peaks in $\Delta_2(N)$ coincide with the discontinuities in the mass spectra. This result represented the first confirmation of cluster shell structure and of the appropriateness of the jellium approach.



Ultraviolet photoemission spectra of ionized copper clusters Cu_N^+ ranging in size from N of 1 to 410 show the energy distribution versus binding energy of photoemitted electrons. These photoemission patterns show the evolution of the 3d band of Cu as a function of cluster size. As the cluster size increases, the electron affinity approaches the value of the bulk metal work function. (Adapted from ref. 10.) **Figure 5**

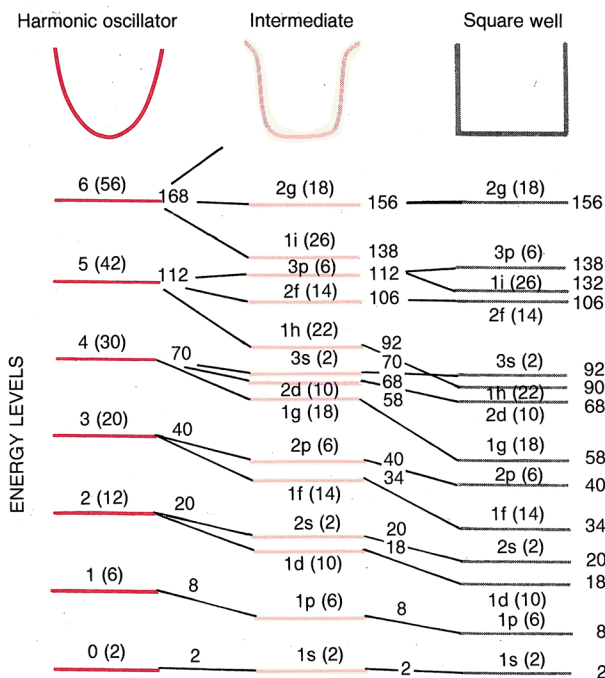
It is expected that closed-shell configurations will lead to spherical clusters. However, for other configurations, one expects Jahn-Teller-type distortions of the kind observed for molecules and nuclei. Ellipsoidal clusters are prevalent for open-shell configurations. Assuming major axes a and b of an ellipse, a distortion parameter η can be defined:

$$\eta = \frac{2(a-b)}{a+b} \quad (5)$$

For alkali clusters with N less than 100, values up to $\eta = 0.5$ are estimated for open-shell clusters using a modified three-dimensional harmonic oscillator model.⁴ This model appears to be adequate to explain many of the features of these systems. The main first-order effects of the ellipsoidal model are energy shifts that are proportional to η . These lead to fine structure in the mass abundance spectra. Although fully self-consistent calculations are not available for all the nonspherical clusters, it is possible to use the electron wavefunction symmetries obtained in simpler models to explore the cluster shapes. For example, as mentioned earlier, for the alkali metal atoms, clusters with N equal to 9 and 10 are prolate, those with N equal to 6 and 7 are oblate and those with N equal to 8 are spherical. These shapes result from considering electronic wavefunctions and differ significantly from shapes derived from geometrical close-packing arguments.

The jellium model assumes that the valence electrons in the clusters are itinerant and interact with a spherically symmetric positive-charge distribution. However, despite screening effects, the electrostatic potential arising from the discrete ions in a cluster of an element such as Na is not expected to be spherically symmetric. Hence, the energy shells and degeneracies given by a spherical jellium should be modified by crystal-field effects. To test the extent of these corrections for alkali metal clusters, a self-consistent local-density pseudopotential approach was applied to a 13-atom face-centered-cubic-type structure and a 15-atom body-centered-cubic-type structure.¹⁹ The resulting calculated charge densities for both cases revealed smeared-out electronic distributions and sufficient screening of the ionic potentials that there was little evidence of bond formation caused by the discrete ionic potentials. The delocalization of the electrons found in this study lends further credence to the jellium picture. The lowest-energy eigenvalues for the respective 13- and 15-atom clusters gave similar energies for the 1s, 1p, 1d and 2s states. Even though the degeneracies of the individual states differed because of the different crystal fields, the eigenvalues were grouped together, and the results were similar to the corresponding values from the jellium model.

Another study compared self-consistent pseudopotential results with the jellium model of simple metal heteroclusters.²⁰ Two cases were investigated, Na_6Mg and Na_8Mg . Again, the electronic charge density distribution was delocalized, and there was little evidence of directional bonding. The central Mg atom in the heterocluster primarily affects the s states, and this gives rise to a small modification of the magic numbers. Because of the level



Energy-level spectra for a three-dimensional harmonic oscillator (red), a square-well potential (gray) and a potential intermediate between the two (pink). The energy-level labels (with degeneracies in parentheses) and the total number of states are given. The intermediate case is representative of the potential found for simple metal clusters. **Figure 6**

lowering caused by the Mg atom, both Na_6Mg and Na_8Mg are closed-shell systems. Moving the Mg from the center to the outermost part of the cluster does not affect the results significantly; this indicates that the Mg atom donates its electrons to the electron gas of the entire cluster. This calculation demonstrated that shell structure still exists in these simple heteroclusters and that the electrons are delocalized. However, if the ratio of non-alkali metal atoms to alkali metal atoms increases, bonds may develop. For Mg and Al, p bands partially hybridize and yield directional bonding. As discussed earlier, the jellium approach can still be appropriate for these systems. Although the best results are expected for large clusters, jellium calculations for small clusters are surprisingly good.

Calculating observable properties

One aspect of the theoretical study of clusters and solids that has lately been receiving considerable attention is the study of excited states. Because most calculations use a local density approximation, there is no theoretical justification for using the eigenvalues to determine excited-state properties. This shortcoming of the local density approximation has been demonstrated convincingly by the fact that calculated semiconductor and insulator bandgaps are consistently underestimated by a large factor, even for cases where computed ground-state properties are in excellent agreement with experiment. For clusters, this is a severe limitation on the theory, because properties such as ionization potentials, polariza-

bilities, optical properties and plasma resonances are best described in terms of excited states.

Because neutral clusters are ionized to make detection possible, knowing the ionization potential is central to the detection process in many experiments. The ionization potential of a cluster can be viewed as analogous to the ionization potential of an atom or the work function of a solid. The local-density approach for atoms gives poor agreement with experimental values of the ionization potential. Things improve when one includes *ad hoc* corrections to the exchange and correlation potentials. Another approach is to associate the ionization potential with the difference in energy between the local-density values for a cluster of size N and one of size $N - 1$. There is reasonable agreement between these two methods, and both reproduce the experimentally observed shell structure. However, the calculated discontinuities in the ionization potential spectra are larger than those observed experimentally.

The experimental studies of cluster polarizabilities have stimulated several theoretical studies. If a classical limit is used, it is expected that the polarizability scales as the cube of the radius, but the value obtained is too small. If a jellium sphere is used, the effective radius is larger, but one still gets an underestimate of the observed polarizability. This underestimation has been studied for both bulk solids and clusters. For the latter case the protrusion of the electron density beyond the jellium sphere effectively increases the radius and the polarizability. However, when this effect is included in addition to the effect of elastic deformation of the jellium background and nonspherical contributions, the theoretical values still fall below the measurements by about 20%. Because the polarizability depends on energy splittings between the ground and excited states, it is felt that the inaccuracy of excited-state spectra is responsible for the lack of agreement with experiment. Based on these arguments, it is not surprising that optical properties and resonance frequencies such as Mie or plasma resonances are difficult to calculate within the local-density approximation.

An approach for calculating excited states has been developed that has been applied successfully to solids and surfaces.²¹ Recently, its extension to clusters²² has demonstrated that this approach can give quasiparticle energies. In particular, Na and K clusters were studied with a jellium approximation. The electronic self-energy was evaluated with the inclusion of local fields, which are substantial because of the confined geometry. The improvements obtained for both the occupied and unoccupied quasiparticle states are encouraging. Some aspects of the new formalism can be applied generally to finite systems. The results for Na and K appear to reconcile the differences between the calculated and measured ionization potentials and to give more accurate electron affinities. This scheme is complex and so far has had limited application. However, improvements and simplifications are likely, and more precise theoretical evaluations of excited states should be possible for a wide range of clusters. This would allow detailed investigation of optical properties, ionization potentials, polarizabilities and a host of other experimentally determined properties.

In the realm of the cluster

Since 1976, when the first sizable congregation of cluster scientists took place in Lyons, France, our experimental and theoretical knowledge have increased rapidly. (One can get a sense of the present rate of growth from the fact that fully half of the references for this article are dated in the current or previous year.) The field is fruitfully interdisciplinary, combining the resources of molecular

and condensed matter physicists and chemists as well as nuclear and materials scientists.

The discovery of shell structure has had a large effect on our theoretical understanding of metallic clusters. Thus far, most work has emphasized this unifying structure that governs the *Aufbau* of the elementary cluster systems. New sources that produce clusters of up to 20 000 atoms permit exploration in the larger size regions, including studies of the supershells dreamed of by the nuclear scientists and even going beyond, into the realm where frozen icosahedral or cubo-octahedral shells²³ of atoms appear. The appearance of these larger structures signals the last stage in the evolution from the droplet of spheroidal jellium to the crystalline geometry of the familiar body-centered-cubic structure of solid sodium. There are also the underlying implications of the dipole resonance experiments that metallic screening among electrons and resistive coupling to thermal vibrations cause the metal cluster to act metallic over the entire range from its embryonic atom form to the bulk.

The influence of cluster studies on our understanding of solid structures is clear, as are the expected extensions to the study of magnetism and superconductivity. Moreover, with more connections yet to be made, we expect that nuclear science and other areas are also likely to reap benefits. Microelectronics systems such as quantum dots, optical detectors and surface devices are already near the realm of the cluster, and further technological benefits from breakthroughs in fundamental and applied science are to be expected.

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