Optical resonances in bimetallic clusters and their relation to the electronic structure

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The optical response of bimetallic clusters of composition \(YA_x\), where \(A\) is an alkali metal and \(Y\) is a monovalent or divalent impurity, is studied by using the random-phase approximation upon a two-step jellium ionic background. With respect to the homologous pure clusters, the optical properties of mixed clusters are found to exhibit conspicuous variations that are directly related to corresponding drastic modifications in the electronic structure induced by the impurity atom. Parallel \textit{ab initio} calculations are performed to test the adequacy of the two-step jellium model.

I. INTRODUCTION

One of the most interesting aspects of metal clusters is that their ground-state properties (e.g., the stability, ionization potentials, electron affinities) exhibit discontinuities as a function of size that are strikingly similar to those observed in corresponding quantities (e.g., in the separation energies for protons and neutrons) in nuclear physics. The observation by Knight and his co-workers that the abundances in the mass spectra of alkali-metal clusters exhibited pronounced peaks or steps at 2, 8, 20, 40, 58, 92, 138, ... atoms, in close resemblance with the magic numbers in nuclear physics, constituted a major development in our understanding of cluster physics. Indeed, it lent support to the jellium-background model and to a view of metal-cluster properties as due primarily to fully delocalized valence electrons that are, however, confined inside the finite volume of the cluster. Thus, the enhanced stability of the magic alkali-metal clusters was explained as an effect of electronic shell structure, just as the enhanced stability of magic nuclei is due to the nuclear shell structure.

The observation of these discontinuities offered the first indication that clusters constitute a link between nuclear physics and condensed matter physics (for a review, cf. Refs. 4–6). Indeed, metal clusters provide an avenue where concepts from nuclear structure and nuclear dynamics can be applied in the electron-volt energy range. In particular, the shell structure in clusters can be studied by considering the effective central potential field that binds the delocalized valence electrons. In analogy with nuclear physics, a Woods-Saxon external potential was first considered, but it soon became apparent that more appropriate central potentials can be constructed self-consistently starting from the jellium-background approximation. In this approach, the ionic lattice is replaced by a uniform, positive, spherical density, while the Coulomb interaction between the delocalized electrons is treated in the local-density approximation (LDA). Then the effective field is specified self-consistently by minimizing the total energy of the valence electrons according to the Kohn-Sham method.

To illustrate how the discontinuities in the ground-state properties relate to the shell structure induced by the effective potential, we have calculated the ionization potentials of pure potassium clusters in the spherical jellium approximation. They are displayed in Fig. 1 along with the corresponding energies of the highest occupied molecular orbitals (HOMO). The largest ionization potentials at 8, 18, and 20 electrons are accompanied by sharp drops, while the HOMO levels exhibit the opposite behavior in keeping with Koopman's theorem. This behavior reflects the filling up of the 1\(p\), 1\(d\), and 2\(s\) electronic shells, respectively. Figure 2 displays the electron affinities for small potassium clusters. Since the added electron goes into the lowest unoccupied molecular orbital (LUMO), the LUMO levels also reflect sharp

\[ \text{FIG. 1. The ionization potentials (IP's) for the pure series K_x calculated in the spherical jellium approximation. The corresponding energies of the 1p, 1d, 2s, and 1f highest occupied molecular orbitals (HOMO) are also shown. The maximum IP's appear when an electronic shell is closed at N = 8, 18, and 20 electrons (N = x). All the IP's have values higher than the bulk work function of potassium at 2.4 eV (dashed line).} \]
FIG. 2. The electron affinities (EA's) for the pure series K$_x$ calculated in the spherical jellium approximation. The corresponding energies of the 1p, 1d, 2s, and 1f lowest unoccupied molecular orbitals (LUMO) are also shown. The minimum EA's appear when an electronic shell is closed at $N = 8$, $18$, and $20$ electrons ($N = x$). All the EA's have values lower than the bulk work function of potassium at 2.4 eV (dashed line).

changes in the electron affinity at the electronic magic numbers 8, 18, 20,…. Thus the ionization potential (electron affinity) and the HOMO (LUMO) levels carry the physics in jellium clusters.

The similarities between metal-cluster and nuclear physics extend beyond the ground-state properties. Indeed, the optical response of metal microclusters exhibits substantial analogies with corresponding photonuclear processes.$^8$ In particular, the photoabsorption in metal clusters proceeds via the excitation of a dipole plasma mode where the valence electrons move collectively against the jellium positive background. This process is quite analogous to the well-known giant dipole resonance in nuclei, where the protons move against the neutrons.$^{10}$

Detailed studies of the photoabsorption profiles in alkali-metal clusters have been carried out using the time-dependent extension of the local-density approximation (TDLDA),$^{11-13}$ or using techniques closely related to the nuclear many-body problem.$^{14-16}$ In particular, the matrix-RPA (random-phase approximation) was adapted$^{14,15}$ to the case of spherical, closed-shell clusters. For specific mass numbers and species, like neutral Na$_{20}$ and Na$_{40}$, this method predicted multipeak photoabsorption profiles, more complex than the simple one-peak profile expected from the Mie theory$^{17}$ for the charge oscillations of a classical metal sphere (ellipsoidal model$^{18,19}$). Such profiles have been recently observed experimentally.$^{18,20}$ They represent quantum size effects due to the discreteness of the single-particle levels and their bunching into electronic shells.

Unlike the ground-state properties, which reflect directly the level bunching into shells, the optical response depends upon energy differences between unoccupied and occupied electronic orbitals, and thus it reflects the shell structure in a less obvious way. However, this paper will show that a well-defined relationship between trends in ground-state properties and trends in excited-state properties can be established as the shell structure varies from the pure to the mixed metallic aggregates.

Indeed, selective changes in the position of single-particle levels can be reflected both in the electronic and in the optical properties of clusters. To this end, a means is needed for altering the electronic structure away from the square-well prototype, familiar from the case of pure alkali-metal clusters. In the case of metallic clusters, an efficient way for inducing modifications in the electronic structure is the alteration of their chemical composition. In particular, with respect to the pure clusters, the impurity in bimetallic clusters, like MgK$_x$ and NaK$_x$, induces unequal shifts in the single-particle levels.$^{21-25}$ Specifically, the s levels are substantially influenced, while the rest of the angular momenta remain relatively unaffected. The associated shifts are drastic and can be reflected in a conspicuous way in concerted variations of both the ground-state properties and the optical properties. The aim of the present paper is to study these modifications and their interconnection. To this end, both molecular methods and nuclear methods, adapted to the case of compound aggregates, will be utilized.

We describe the theoretical formulation in Sec. II. In Sec. III we compare the molecular and jellium approaches. The results are presented in Sec. IV, and the conclusions are drawn in Sec. V.

II. THEORETICAL TOOLS
AND METHODOLOGY

A. Two-step jellium background

Before proceeding to study the properties of mixed clusters, we need to develop an adequate description of the associated static, effective potentials. Apart from the calculation of ground-state properties, the effective potentials are needed as an input into the matrix-RPA within the local-density approximation utilized here. Specifically, the influence of the average field upon the RPA equations is manifested through the energy differences from the unoccupied to the occupied single-particle orbitals (particle-hole transitions). For mixed clusters, such effective potentials can be determined within the framework of a modified jellium background.

For homonuclear clusters, the effective potential is determined by replacing the ionic charges by a homogeneous positive background of density $n_0$ which, in the absence of any other information, is assumed to have the bulk value $Z/n_0$ (Z being the atomic valence and $n_0$ the atomic volume). The radius $R$ of the positive background is determined by the number $N_a$ of atoms in the cluster,

$$\frac{4\pi}{3}R^3 n_0 = N_a Z = N.$$

(1)

$N$ is naturally the total number of delocalized electrons in the cluster.

Since metal clusters occupy a finite volume, the rela-
tive spacing of the electron energy levels will of course depend upon the value of \( n_0 \). Empirical evidence suggests that, for pure sodium and potassium clusters, the bulk values of \( n_0 \) are good enough. However, there is no apparent reason why the cluster ion density \( n_0 \) should be the same as the bulk density. A more refined procedure would choose the value of \( n_0 \) in small clusters in such a way that the level spacings calculated in the jellium model correspond as closely as possible to those obtained from self-consistent-field-linear combination of atomic orbitals–molecular orbitals (SCF-LCAO-MO) calculations on optimized cluster geometries. Then, comparisons can be made with clusters of different sizes to see how the average background density \( n_0 \) evolves and approaches the bulk value.

For a compound cluster containing the heteroatom (impurity \( I \)) at the center of the otherwise homonuclear host (\( H \)) cluster, the positive background \( n_+ \) will be modified as follows:

\[
n_+ = n_0^I \theta(R_I - r) + n_0^H \theta(r - R_I) \theta(R_H - r),
\]

where \( \theta(R - r) = 0 \) for \( r > R \) and 1 for \( r < R \) (see Fig. 3).

The use of the two-step jellium model (2) is particularly useful in describing large heteroclusters, since \textit{ab initio} methods of the type described earlier are restricted to small clusters due to limitations of the present computational resources.

In the case of the two-step distribution (2), an initial choice for the electronic densities could be the corresponding bulk values. However, although this choice preserves the overall trend in the abundance spectra, it leads to significant discrepancies with the experimental observations in the case of divalent impurities.22 Best known is the case of the series MgK\( x \), where this procedure predicts strong abundance maxima for both MgK\( 6 \) and MgK\( 8 \), even though only MgK\( 8 \) exhibits a maximum in the experimental abundances.26

In the present work, we will adopt a more flexible approach, and, we will assign to the density \( n_0^I \) of the divalent impurity a set of varying values, while retaining the bulk value for the alkali-metal atoms. A comparison with the observation for both the ground-state and optical properties will determine the best values for the model. In parallel, comparison with molecular-orbital calculations can yield information about the adequacy of the assumed geometrical arrangement for the ionic cores.

**B. Random-phase approximation**

The description of the collective excitations of bimetallic clusters, which we will present below, follows closely the method used to describe plasma resonances in pure alkalii-metal clusters.14,18 A discrete particle-hole basis is constructed out of the single-particle energies for the Hamiltonian,

\[
H_0 = T + U(r),
\]

where \( U(r) \) is the static effective potential resulting from the two-step jellium background and \( T \) is the kinetic energy of the valence electrons. Then the total Hamiltonian \( H = H_0 + V \), sum of \( H_0 \) and of the residual particle-hole interaction \( V \) specified in the local-density approximation (LDA), is diagonalized using the matrix-RPA (for details, cf. Ref. 15).

The RPA eigenstates \(| \ell \rangle \) are formed as a linear superposition of particle-hole excitations in terms of the forward-going and backward-going amplitudes. Since the RPA preserves the Thomas-Reiche-Kuhn (energy-weighted) sum rule \( S(E_1) = NH^2e^2/2m \), the dipole transition probabilities \( B(E1, 0 \rightarrow n) \) and associated eigenvalues \( E_n \) obey the relation

\[
\sum_n f_n = 1,
\]

where the oscillator strengths \( f_n \) per delocalized electron are defined as

\[
f_n = \frac{E_n B(E1, 0 \rightarrow n)}{S(E1)}.
\]

This result is also valid for the unperturbed particle-hole excitations.

**C. Molecular calculations**

The electronic structure calculations were carried out within the linear combination of atomic orbitals–molecular orbitals (LCAO-MO) approach.27 The molecular wave function \( \Psi \) is expressed as a linear combination of atomic orbitals \( \phi_k \) centered at the atomic sites \( k \). The orbitals \( \phi_k \) are themselves expanded as a sum of the Gaussian functions \( g_j \),

\[
\Psi = \sum_k a_k \phi_k = \sum_k a_k \sum_j c_{kj} g_j = \sum_{kj} d_{kj} g_j.
\]

The coefficient \( d_{kj} \) are determined via a solution of the
Rayleigh-Ritz equation

\[ (H - E)\Psi = 0, \]

where \( H \) is the many-body Hamiltonian consisting of the kinetic energy \( T \), the ionic attraction term \( V_{\text{ion}} \), the electronhartree repulsion \( V_H \), and the electron-exchange-correlation term \( V_{\text{xc}} \), namely,

\[ H = T + V_{\text{ion}} + V_H + V_{\text{xc}}. \]

In all our studies, the exchange-correlation contributions have been included within the density-functional approach.\(^9\) Equation (7) then reduces to the Kohn-Sham equations,

\[ \left(-\frac{1}{2} \nabla^2 + V_{\text{ion}} + V_H + V_{\text{xc}}^\sigma\right) \Psi_{\sigma}^\nu = \epsilon_{\nu}^\sigma \Psi_{\sigma}^\nu, \]

where \( \sigma \) is the spin index (up or down) and \( \nu \) is the eigenvalue index.

We have used the form of the exchange-correlation potential proposed by Ceperley and Alder.\(^{29}\) Further, the inner cores have been replaced by norm-conserving nonlocal pseudopotentials. The particular form of pseudopotentials we have used are the ones proposed by Bachelet, Hamann, and Schlüter.\(^{30}\) These are based on accurate local-density calculations on atoms, with optimum transferability, and their parametrized form is easily adaptable for molecular applications.

To carry out electronic structure calculations, one needs the Gaussian basis functions \( g_j \). Since we are using pseudopotentials, the available Gaussian basis functions for Hartree-Fock and other all electron studies are not appropriate. We therefore developed our own basis sets by solving the atomic equation on a numerical mesh. The numerical atomic functions were fitted nonlinearly to a combination of Gaussian functions. For Na, K, Mg, and Zn, the basis sets consisted of \((3s,2p)\), \((4s,3p)\), \((4s,2p)\), and \((4s,2p,5d)\) basis functions, respectively. All the basis sets were not contracted. The basis sets were tested by comparing the one-electron levels and the total energy based on the basis sets with the corresponding quantities obtained via numerical integration of the Schrödinger equation. The basis sets were also tested for their overcompleteness by carrying out atomic calculations with an extra set of basis functions at varying distances. The changes in total energy were minimal.

Using the above Gaussian functions, Eq. (9) was solved self-consistently. The total energy was calculated via the expression\(^{31}\)

\[ E = \sum_{\sigma, \nu} \langle \Psi_{\sigma}^\nu \mid \left(-\frac{1}{2} \nabla^2 + V_{\text{ion}}\right) \Psi_{\sigma}^\nu \rangle + \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r - r'|} \, dr \, dr' + \int \epsilon_{\text{xc}}(r) \rho(r) \, dr + \sum_{1 \leq i < j \leq N} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}, \]

where \( \rho(r) = \sum_{\nu} \langle \Psi_{\nu}^\nu \mid \Psi_{\nu}^\nu \rangle \) and \( \rho(r) = \sum_{\sigma} \rho_{\sigma}(r) \) denotes the electron density at the point \( r \). \( \epsilon_{\text{xc}}(r) \) denotes the exchange-correlation energy per electron, and \( Z_i \) is the charge of the ions located at \( \mathbf{R}_i \). The ground-state geometries were obtained by minimizing the total energy for given symmetry constraints.

III. COMPARISON OF MOLECULAR AND JELLUM CALCULATIONS

To test the reliability of the two-step jellium model, we have carried out parallel molecular calculations and have compared the electronic structures resulting from the two approaches. Specifically, we present here results for the mixed aggregates MgK₈, ZnNa₈, and MgKr₈. In the case of the molecular calculations, the geometry was assumed to be a centered cubic for MgK₈ or ZnNa₈ and a centered octahedron for MgKr₈. For the jellium calculations, the densities \( n_{\text{jellium}}^\sigma \) and \( n_{\text{jellium}}^{1s} \) were assumed to be equal to the corresponding bulk values.

For these two geometries, the molecular electronic configurations are of the type \((1a_{1g})^2 \) \((1t_{1u})^6 \) \((2a_{1g})^2 \) and \((1a_{1g})^2 \) \((1t_{1u})^6 \), respectively. Comparison with the jellium calculations is based on the correspondence \( 1s \rightarrow 1a_{1g}, 1p \rightarrow 1t_{1u}, 2s \rightarrow 2a_{1g}, \) and \( 1d \rightarrow (1d_e + 1d_s) \). Generally, the gap inside the molecular \( d \) manifold is much smaller than the gap between the major shells, and it can be overlooked for the purpose of the present comparison. To illustrate the validity of this correspondence between the orbital levels, we have decomposed the molecular wave functions in angular-momentum orbitals with respect to the ionic charge center. For the case of ZnNa₈, the coefficient of the spherical harmonic with the maximum contribution \( C_L \) is listed in Table I. Even for the least favorable case of the \( d \) orbitals, the corresponding coefficient \( C_L \) is very large, namely, 0.980.

Table I also lists the energy spectra. It is apparent that the agreement between molecular and two-step jellium calculations is very good. In particular, both calculations reproduce the downward shift of the 2s level below the 1d level, and thus are able to account for the principal experimental finding, namely the appearance of the new magic number \( N = 10 \) electrons.\(^{32}\)

This agreement between electronic configurations persists also in the case of MgK₈ and MgKr₈, as Table II and Fig. 4 illustrate, respectively. Such an agreement between molecular and jellium methods lends support to the usefulness of the two-step jellium background as an alternative approach in describing metal heteroclusters, a fact particularly relevant in the case of larger mass numbers \( (> 10) \) where computer limitations restrict the applicability of ab initio methods.

<table>
<thead>
<tr>
<th>Molecular</th>
<th>Jellium</th>
</tr>
</thead>
<tbody>
<tr>
<td>eV</td>
<td>eV</td>
</tr>
<tr>
<td>(1a_{1g} )</td>
<td>-7.41</td>
</tr>
<tr>
<td>(2a_{1g} )</td>
<td>-3.89</td>
</tr>
<tr>
<td>(2a_{1g} )</td>
<td>-2.81</td>
</tr>
<tr>
<td>(1d_{1} )</td>
<td>-1.85</td>
</tr>
</tbody>
</table>
TABLE II. Molecular vs jellium levels for MgK$_8$.

<table>
<thead>
<tr>
<th>Molecular</th>
<th>eV</th>
<th>Jellium</th>
<th>eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a$_{1g}$</td>
<td>-4.65</td>
<td>1s</td>
<td>-4.85</td>
</tr>
<tr>
<td>1b$_{1u}$</td>
<td>-2.44</td>
<td>1p</td>
<td>-2.86</td>
</tr>
<tr>
<td>2a$_{1g}$</td>
<td>-1.87</td>
<td>2s</td>
<td>-2.09</td>
</tr>
<tr>
<td>1d$_{4}$</td>
<td>-1.30</td>
<td>1d</td>
<td>-1.50</td>
</tr>
</tbody>
</table>

In spite of the explanation of the $N = 10$ magic number, both the calculations presented in this section fail to account for additional important features of the observed mass spectra. In particular, they fail to account for the sole observation of an abundance peak at $N = 10$ and the simultaneous absence of a peak at $N = 8$. This is because both calculations exhibit comparable gaps between the 1p and 2s levels and between the 2s and 1d levels, and thus predict an abundance peak for MgK$_8$ and ZnNa$_8$ as important as the peak for MgK$_8$ and ZnNa$_8$. This is in clear disagreement with the experimental observations for ZnNa$_8$ and MgK$_8$ (a summary of the available experimental abundance maxima for mixed aggregates is compiled in Table III).

What this discrepancy indicates is that the actual 2s level is probably situated even lower than the present calculations suggest, probably close or below the 1p level. Since the second differences, $\Delta_2 = E(YA_{x+1}) + E(YA_{x-1}) - 2E(YA_{x})$, reflect the energy gaps of the electronic spectrum, this conclusion is independent of the method considered, jellium or molecular. In the framework of the molecular orbital calculations, a better agreement between theory and experiment could be reached by considering different geometric configurations. In the framework of the two-step jellium background, it will suffice to consider the electronic density of the divalent impurity as a variable and adjust it to produce the additional necessary downward shift for the 2s level. This approach will be followed in Sec. IV, where a detailed comparison between the jellium results and the available experimental data for both abundances and photoabsorption spectra will be presented.

This methodology is supported by the jellium calculations of Refs. 22 and 23 which found that, although the global trends presented in the abundance maxima in Table III (e.g., the disappearance of the magic $N=8$ and the appearance of the magic $N=10$) depended upon the difference of the electronic densities between impurity and host, and could be understood using bulk $r_s$ values, the detailed behavior of a given aggregate with a divalent impurity was systematically misplaced in their calculated evolutionary sequence.

IV. RESULTS AND DISCUSSION

A. Monovalent impurity: The series NaK$_x$ and RbK$_x$

We will first consider the case of a monovalent alkali impurity, and in particular the sequence NaK$_x$. We compare the properties of NaK$_x$ with those of pure K$_x$. Experimentally, there exist some measurements of the abundances of NaK$_x$ as compared to the abundances of K$_x$\textsuperscript{2,33} We begin with a review of the available experimental data before describing the corresponding theoretical calculations.
1. Single-particle levels

As reported in Refs. 2 and 33, the presence of the Na impurity produces relative differences in the mass spectra of the doped NaK$_x$ as compared to the series of the pure K$_x$. These differences are not as extreme as in the case of the series MgK$_x$ or ZnNa$_x$, where the divalent dopant produces a new magic number for $N = 10$ electrons. Indeed, eight electrons is a well-defined magic number for both NaK$_x$ and K$_x$. The relative differences appear in the area of 18-20 electrons. In particular, the rise in intensity to NaK$_{19}$ (20 electrons) is strongly peaked in contrast to the pure K$_x$ clusters. Moreover, in the case of Cs-doped clusters (impurity of smaller electronic density), an increase in intensity is observed up to CsK$_{17}$ (18 electrons), followed by a drop at CsK$_{18}$.

These observations can be interpreted on the basis of the shell model as due to a competition of the 1d (18 electrons) and 2s (20 electrons) shell closures. Our calculations using the two-step jellium background, with the dopant occupying the central region, supports this interpretation. Figure 5 displays the second differences $\Delta_2$ for the series of pure K$_x$ versus the compound series NaK$_x$ and RbK$_x$. We have used the values of the bulk for $r_1^+$, namely 4.00 a.u. for sodium (for potassium this value is 4.86 a.u., for rubidium it is 5.20 a.u.). Going from K$_x$ to NaK$_x$, the peak for $N = 18$ electrons disappears, while the $N = 8$ peak remains unaffected, and no $N = 10$ peak does appear. For the series RbK$_x$, the $N = 18$ peak is enhanced. These trends are in good agreement with the experimentally observed abundances\textsuperscript{2,33} described earlier (like cesium, rubidium has a lower electronic density than potassium).

Figure 5 also displays the corresponding positions of the 1s, 1p, 1d, 2s, and 1f levels both for $N = 8$ and for $N = 20$ electrons ($N = x + 1$, in the case of NaK$_x$ and RbK$_x$). The corresponding potentials are displayed in Fig. 6.

A conspicuous effect of the heteroatom at the center\textsuperscript{34} is the dramatic change it can cause in the effective central potential that binds the delocalized electrons compared to the case of pure clusters. Specifically, for $n_l^c > n_l^H$ (as is the case with NaK$_x$), a depression centered at the origin develops in the potential. This depression results in unequal shifts in the single-particle levels. The bound single-particle levels that are most influenced are the $s$ orbitals, while the $p$ and $d$ orbitals remain comparatively unchanged. This is a consequence of the $\hbar^2 l(l+1)/2mr^2$ repulsive centrifugal potential that insulates the higher angular momenta from the narrow depression. The extent of the shift sustained by the $s$ levels depends on both the difference in the electronic densities and on the size of the aggregate. This is seen from Fig. 5, where the large shifts of the $s$ levels are clearly exhibited. In the vicinity of $N = 8$ electrons the shift of the $2s$ state is not strong enough, and the $2s$ level remains above the $1d$ level. As a result, no $N = 10$ electrons magic number appears. On

![Figure 5](image1.png)

**FIG. 5.** Jellium second differences for the compound series RbK$_x$ and NaK$_x$ ($N = x + 1$) compared to the pure series K$_x$ ($N = x$). Bulk Wigner-Seitz radii (as indicated) were used both for the host potassium and for the monovalent impurities. The peak at $N = 18$ electrons competes with the peak at $N = 20$. An impurity with a lower electronic density (higher Wigner-Seitz radius) favors the $N = 18$ peak and vice versa in accordance with the observations for the mass spectra (Refs. 2 and 33). Notice that the peak at $N = 8$ is not influenced. This behavior is explained by the relative shift, induced by the impurity, of the $2s$ level with respect to the other orbitals, as illustrated in the left and right columns. The $2s$ level is more influenced at $N = 20$ than at $N = 8$. Left column: the jellium single-particle levels at the size $N = 8$ electrons (solid squares: 1s; solid circles: 2s; open circles: 1p; open squares: 1d; open diamonds: 1f). Right column: the jellium single-particle levels at $N = 20$ electrons.

![Figure 6](image2.png)

**FIG. 6.** The jellium effective potentials at $N = 8$ and $N = 20$ electrons for the monovalent impurities Na and Rb in a potassium host. The dashed lines correspond to the pure potassium K$_x$ and K$_{20}$ cases. For an impurity with a larger electronic density (like Na), a depression develops at the origin. On the contrary, for an impurity with a smaller electronic density (like Rb), a hump develops at the origin. Due to less efficient screening, the influence of the impurity is more pronounced at $N = 20$ than at $N = 8$ in agreement with the relative shifts of the $2s$ level (cf. the corresponding single-particle spectra in Fig. 5).
the contrary, in the vicinity of \( N = 20 \) electrons, the \( 2s \) level is shifted further down and is slightly lower than the \( 1d \) level. As a result, the \( N = 18 \) electrons magic number does not appear in the sequence \( \text{NaK}_x \).

In the case of a dopant with a smaller electronic density (the case of \( \text{CsK}_x \) or \( \text{RbK}_x \)), the opposite trends develop. Indeed, a hump (local maximum) develops now at the center of the effective potential and the \( 2s \) level is shifted upwards favoring the \( N = 18 \)-electrons peak over the \( N = 20 \)-electrons peak.

2. Ionization potentials

The movement of the \( 2s \) level is also reflected in the ionization potentials for the series \( \text{NaK}_x \) and \( \text{RbK}_x \) (cf. Fig. 7), as compared to the pure sequence \( \text{K}_x \) (cf. Fig. 1). Indeed, the I.P. does not show a step at \( \text{NaK}_{17} \), in agreement with the abundances. For the case of the less dense impurity, the step at \( \text{RbK}_{19} \) is missing.

Otherwise, it is to be noticed that the value of the I.P. is almost independent of the impurity. This is because the ionization potential reflects the HOMO levels, whose energy changes very little due to the impurity. In particular, for \( 4 \leq x \leq 7 \), the HOMO is the \( 1p \) level, while for \( 8 \leq x \leq 17 \), the HOMO is the \( 1d \) level. This trend is in agreement with the experimental results on \( \text{K}_x \) and \( \text{NaK}_x \) presented in Ref. 35.

3. Optical response

It has been found\(^{15} \) that the split-plasmon that characterizes the photoabsorption profiles of homonuclear \( \text{Na}_{20} \) and \( \text{K}_{20} \) clusters can be treated as a two-level model due to a degeneracy between the collective plasmon and a particular \( 2s \rightarrow 3p \) particle-hole transition. In the case of the compound \( \text{NaK}_{19} \), the impurity at the center shifts the \( 2s \) level downwards, but barely affects the \( 3p \) level, while, at the same time, the position of the plasmon remains unchanged. As a result, the energy of the \( 2s \rightarrow 3p \) transition increases (cf. Fig. 8), and it is to be expected that the degree of the splitting in the photoabsorption spectrum will be affected by the presence of the Na dopant. Indeed, matrix-RPA calculations for \( \text{K}_{20} \) and \( \text{NaK}_{19} \) are displayed in Fig. 9. In the case of \( \text{K}_{20} \), the plasmon is split into two components, while in the case of \( \text{NaK}_{19} \) there appears one dominant line with 80% of the Thomas-Reiche-Kuhn sum rule. In the case of \( \text{RbK}_{19} \), the \( 2s \rightarrow 3p \) transition becomes comparatively smaller, and the extent of plasmon splitting is more pronounced, as Fig. 9 illustrates.

We have shown that the introduction of a monovalent \( Y \) impurity modifies the electronic structure of the compound \( \text{YK}_x \) with respect to the pure \( \text{K}_x \) series. In particular, in the vicinity of 20 electrons, the \( 2s \) level is

FIG. 7. The ionization potentials for the compound series \( \text{RbK}_x \) and \( \text{NaK}_x \) \( (N = x + 1) \). Compared to the pure \( \text{K}_x \) (cf. Fig. 1), only one step appears in the range \( N = 18-20 \). \( N = 18 \) is favored over \( N = 20 \) for \( \text{RbK}_x \), while the opposite holds for \( \text{NaK}_x \).

FIG. 8. The variations of the \( 2s \rightarrow 3p \) transition that splits the plasmon in the case of pure \( \text{K}_{20} \), but not in the case of the mixed \( \text{NaK}_{19} \). The associated jellium potentials are also shown. The dashed lines indicate the HOMO levels. The bulk Wigner-Seitz radii that were used are also indicated.

FIG. 9. RPA oscillator strengths for the compound \( \text{RbK}_{19} \), \( \text{NaK}_{19} \), and the pure \( \text{K}_{20} \). Bulk Wigner-Seitz radii were used.
strongly shifted, while the 1d and the np levels remain relatively unaffected. This movement of the 2s level was shown to be reflected both in the ground-state properties as well as in the photoabsorption of the mixed aggregates.

B. Divalent impurity: The sequence ZnNa₈

1. Magic numbers

As discussed earlier the central depression in the potential due to the dopant shifts the 2s level, but leaves the 1p and 1d levels relatively unaffected. The deeper the depression, the deeper the 2s state is pushed down. If it is shifted below the 1d level, a new magic number for N = 10 electrons can appear for the series BA₈, where B denotes a divalent impurity \((N = z + 2)\). As shown in Fig. 10 (right column), this has happened already for \(r_f^B = 3.00\) in the series BNa₈. In this case, the compound aggregate is spherical, like the case of Na₈, and in sharp contrast to the prolate Na₆. The competition of the peaks between \(N = 8\) electrons and \(N = 10\) electrons in the abundance spectra, however, is determined by the relative position of the 2s state with respect to both the 1d and 1p levels. Figure 10 displays the evolution of the second differences \(\Delta_2\) in the total energies of the BNa₈ aggregates, when the Wigner-Seitz radius of the central impurity varies from 3.00 to 1.15 a.u. (for the corresponding potentials, cf. Fig. 11). A lower \(r_f^B\) favors the \(N = 10\) peak. For \(r_f^B = 1.15\) the \(N = 8\) peak has disappeared, in agreement with the experimental data on ZnNa₈ (Ref. 26) (for comparison, the bulk Wigner-Seitz radius of Zn is 2.31). For MgNa₈, the experiment exhibits two equally sized peaks. From an inspection of the trend in the second differences displayed in Fig. 10, this latter compound seems to correspond to \(r_f^B = 1.90\) (for comparison, the bulk Wigner-Seitz radius of Mg is 2.65). Figure 10 also displays for \(N = 10\) electrons the energy levels for the 1p, 1d, and 2s single-particle states (right column). The downward shift of the 2s level between the 1d and the 1p levels is well noticeable and is in agreement with the competition of the \(N = 8\) and \(N = 10\) peaks in the corresponding plots for the second differences.

From a comparison of the experimental mass spectra for ZnNa₈ and the second differences resulting from a two-step jellium model for the series BNa₈, we infer that the best value for the Wigner-Seitz radius of the Zn impurity is 1.15 a.u. This value is substantially different from the corresponding bulk value. For the Wigner-Seitz radius of Na, we retain the bulk value of 4.00 a.u. With this choice then, we proceed to calculate the optical response of ZnNa₈, and compare it to the observation.  

2. Photoabsorption

ZnNa₈ offers another typical example of the influence of the impurity upon the photoabsorption profiles. The photoabsorption cross section of this cluster has recently been measured by Kappes et al. A double peak has

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**FIG. 10.** Left column: jellium second differences for the series BNa₈ \((N = z + 2)\), where B denotes a divalent impurity whose Wigner-Seitz radius varies from 3.00 to 1.15 a.u., as indicated in the figure. Right column: jellium single-particle spectra for BNa₈ corresponding to the different electronic densities of the divalent impurity (solid circles: 2s; open circles: 1p; open squares: 1d). The downward shift of the 2s orbital between the 1d and the 1p levels is apparent, and correlates with the variations in the second differences. The \(r_f^B\) that best reproduce the observations (cf. Table III) for the mass spectra of ZnNa₈ are 1.15 and 4.00.

**FIG. 11.** Jellium potentials for BNa₈, where B stands for a divalent impurity whose Wigner-Seitz radius varies as indicated from 4.00 to 1.15 a.u.
been observed: the higher component lies at 2.97 eV and carries a smaller amount of the strength than the lower component at 2.63 eV. Figure 12 displays the RPA response for the system BNa$_8$ for two different values of $r^d_s$. For $r^d_s = 1.60$, one single line at 2.76 eV carries 62% of the TRK sum rule. In the case of $r^d_s = 1.15$, the single line is fragmented into three smaller lines. Two of these lines at higher energies (at 2.87 eV) are closely spaced and will appear as one peak after the broadening that accounts for the experimentally observed widths. Between the two of them, they carry 26% of the total strength, while the stronger line at 2.57 eV carries 42% of the strength. The variations in the photoabsorption profiles displayed in Fig. 12 depend again upon the extent of the shift sustained by the s levels. In particular, the fragmentation at the value $r^d_s = 1.15$ is due to a degeneracy that occurs between the plasmon and the $2s \to 2p$ and $1p \to 3s$ particle-hole transitions (cf. Fig. 13). A very strong shift downwards supplied by the value $r^d_s = 1.15$ is needed for this degeneracy to develop. As discussed in the earlier paragraph, the same shift accounts sufficiently well for the trend in the observed abundances of the series ZnNa$_8$.

FIG. 13. The variations of the $2s \to 2p$ and $1p \to 3s$ transitions that develop as the electronic density of the divalent impurity changes. These transitions split the plasmon when the Wigner-Seitz radius of the impurity is 1.15 a.u. (cf. Fig. 12). The associated jellium potentials are also shown. The dashed lines indicate the HOMO levels. The bulk Wigner-Seitz radius of Na that was used is also indicated.

V. CONCLUSION

We conclude that a two-step jellium background with the background density for the central region substantially different from the bulk value can describe sufficiently well both the optical properties and the abundances of compound clusters possessing a divalent impurity. In the case of an alkali-metal impurity, use of the bulk value seems to suffice. Specific examples have been presented on how the influence of the impurity can be accounted for within a unified framework by considering the modification of the effective average field. Approaches adapted from the nuclear many-body problem (matrix RPA) can then be immediately applied to treat the photoabsorption of compound clusters in analogy with the case of pure clusters. A strong correlation between relative differences in the electronic structure and relative differences in the optical response was found.

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10Å. Bohr and B.R. Mottelson, Nuclear Structure (Benjamin, Reading, MA, 1975), Vol. II.
32That the presence of a divalent impurity results in the reordering of the 2s and 1d levels, so that a shell closure occurs at N = 10 electrons (the new magic number) instead of the usual N = 18, was originally described in Ref. 21. In particular, Ref. 21 calculated the single-particle spectra of the two aggregates MgNa₈ and MgNa₉ using ab initio molecular methods.
34The impurity atom in all cases here is assumed to be in the center. In the case of several K impurities in Na, however, there is experimental and theoretical evidence that potassium tends to be on the surface [P. Ballone et al., Europhys. Lett. 8, 73 (1989)].
36M.M. Kappes et al. (unpublished).