Low-energy excitonic resonances in metals.
II. Cluster calculations for divalent impurities in Li metal

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Recent spectroscopic studies of dilute and concentrated divalent impurities in alkali metals identify an important new type of local-excitation phenomenon. The results are not consistent with simple band-theory models for alloys. Instead they suggest that *locally* excited configurations of impurities occur in the metallic host. These local excitations are resonant with the band-to-band continuum of the host, and their excitation energies are significantly red-shifted from those of the free atom. Chemically similar impurities absorb light at approximately the same frequency in a given host. These local excitations seem to persist in the perfect divalent metal as well. A variety of line shapes apparently derived from Fano-like interference between the local excitation and the host conduction band is observed. We describe a theory of these phenomena based upon cluster calculations, including many-body corrections.

I. INTRODUCTION

Recent experiments appear inconsistent with the traditional one-electron description of the low-energy fundamental optical behavior of metals. These phenomena are discussed in the preceding paper by Bakshi, Denton, Flynn, Boisvert, and Kunz,[1] referred to as paper I in the following. Specifically, the observations suggest that the photoexcited electron and hole created in the optical event can interact strongly in the final state to produce an excitonic resonance which, in some cases at least, dominates the optical spectrum. Two-particle phenomena of this type cannot be mimicked by a one-electron formulation of the optical problem. Consequently, the results are potentially of considerable importance. If the two-particle interpretation is correct, it will be necessary to modify the present description of all excitation phenomena in metals, particularly those which depend on single-particle operators and hence on electron-hole overlap.

In this paper we develop a theory of excitation processes in which local excitations of an impurity in the metal are coupled to the conduction-electron liquid. This approach correlates and interrelates phenomena in three separate areas. The first of these is the theory of shallow levels associated with impurities. The second area concerns the interband spectra of metals. The third area is the "x-ray-edge" problems for metals. Our primary emphasis in this paper is on the theory of shallow impurity levels. In the following we briefly describe the experimental results which have prompted the theoretical studies. In the next section we describe theories of the ground- and excited-state electronic structure of alloys which permit the calculation of impurity spectra in the (0.5—5)-eV energy range. We show how to include electronic correlations in the two-carrier processes. The spectral features of special interest here arise when the excited electron and valence hole resonate together in the impurity cell, owing

to their mutual Coulomb attraction, as screened by the metallic conduction electrons. We will make the connection between those processes and the interband spectra of pure metals. The relationship with the x-ray-edge problem in metals will also be noted.

Conventional treatments of the valence excitation spectra in metallic alloys, whether based upon rigid-band concepts or on more self-consistent methods such as the coherent potential approximation (CPA), involve delocalized single-particle orbitals.[2] In such theories, the photon creates a stationary many-electron excited state in which a hole exists in a previously occupied one-electron orbital and an electron occupies a formerly unoccupied orbital, both of which extend, in principle, throughout the metal. The resultant excitation spectrum, if these states are modeled by single Slater determinants, is determined by the joint density of one-electron states and the orbital symmetry of the levels involved.

It is our belief that this simple model is often in error and that, in a number of practical examples, deviations from these simple predictions are easily observable. Consider first a physical situation in which an isolated impurity attracts band electrons so strongly that a photohole is bound below the conduction-band bottom; it is therefore localized at the impurity. Metals must preserve local electrical neutrality in the steady state. Therefore the conduction band deforms in such a way that it localizes an additional screening electron at the impurity site, thereby neutralizing the localized hole. It follows that the excitation produces two carriers bound together at the impurity site. The electron-hole overlap and the optical matrix elements must both be significantly modified by this localization process.

Our present interest lies in a slightly more complicated phenomenon. In the preceding example the electron localization is driven by the hole localization. The latter was presumed to be a one-electron process arising from the

fact that the active orbital lies below the conduction-band bottom. To extend these ideas one must note that the electron localization makes the impurity site more favorable for the hole, and may itself bind a hole which would otherwise propagate away through the metal. In this situation the electronic configuration contains a localized electron and a localized hole which both derive from propagating orbitals of the unexcited system. This is specifically a two-carrier effect, which has no analog in single-particle theory. Weaker interactions might possibly give rise to a two-particle *resonance,* of a character similar to the bound system.

Illustrative examples in which such localization occurs are reported by Denton et al.[3,1] In one case, Mg impurities are placed substitutionally in simple metals such as Li. Dilute solutions of Mg impurities in Li metal are body-centered cubic (bcc). In free space the Mg atom absorbs light at 4.3 eV by the transition $3s^2 \rightarrow 3s\,3p$. It is observed that in Li-Mg alloys this process remains well defined, but is broadened to a width of ~ 0.5 eV and red-shifted to 2.8 eV. The sharpness indicates that the $3p$ state persists for some time in degeneracy with the $2s$-like Li conduction orbitals. A scheme of electronic levels for Li-Mg is shown in Fig. 1. Work by Inglesfield,[4] confirmed in our present calculations, shows that the doubly occupied Mg $3s$ state lies within the occupied Li Fermi sea [Fig. 1(a)]. Figure 1(b) shows that, upon excitation, the occupied $3s$ level may drop below the bottom of the Li Fermi sea and the $3p$ excited level lies within it. Finally, Fig. 1(c) shows one of the excitations of the Li Fermi sea which is degenerate with the Mg $3s^2 \rightarrow 3s\,3p$ excitation. Denton et al.[3] and Flynn and Kunz[5] give thermodynamic and spectroscopic arguments to justify this picture. Paper I contains results for Mg and also other impurities such as Zn and Ca in Li. This paper describes methods by which the spectral line positions may be calculated.

We mention finally that the studies are made possible by state-of-the-art computer programs, implemented on high-speed computers. In our work the programs are self-consistent unrestricted—Hartree-Fock (UHF) cluster
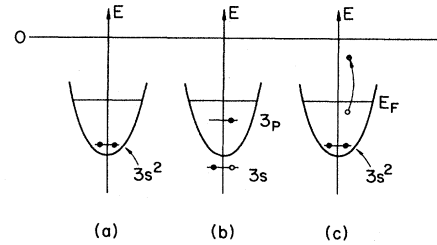

FIG. 1. Sketch of the ground and excited electronic structure of divalent impurities in Li metal, illustrated for Mg impurities. In panel (a) the ns^2 ground-state orbitals are shown within the Li valence band. In panel (b) the excited configuration has the excited np state lying within the Li valence band and the remaining occupied impurity ns level below the Li valence band. Panel (c) indicates a band excitation which is resonant with the impurity excitation. A resonance in which the excitations depicted in (b) and (c) mix probably accounts for the optical line shape observed. It is not necessary that the ns orbital actually be bound below the band bottom, as in panel (b), for this mechanism to occur.

programs augmented by explicit calculation of correlation corrections by means of many-body perturbation theory (MBPT). These programs are implemented upon an FPS 164 scientific computer system operating through a VAX 11-750 Computer at the University of Illinois Materials Research Laboratory. The programs are designed to take advantage of the parallel-pipelined architecture of the FPS 164 and to gain significantly from its speed. Even so, the calculations described here require significant amounts of computer time.

II. THEORETICAL METHODS AND COMPUTATIONAL DETAIL

These studies employ the UHF method as a starting point. The normal nonrelativistic Hamiltonian is

$$H = -\sum_{i=1}^{n} \frac{\hbar^2}{2m}\nabla_i^2 - \sum_{i=1}^{n}\sum_{I=1}^{N}\frac{e^2 Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i,j=1}^{n}{}' \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{I,J=1}^{N}\frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} \ . \tag{1}$$

We use lower-case letters to designate electronic properties and upper-case letters for nuclear properties. The ith electron has coordinate $\mathbf{r}_i$ ($\mathbf{x}_i$ including spin), mass m, and charge e. The Ith nucleus has atomic number Z_I and position $\mathbf{R}_I$. It is assumed that the nuclei are infinitely massive; the Born-Oppenheimer and Frank-Condon approximations are used as needed. In principle, one must solve the n-electron Schrödinger equation:

$$H\Psi_\alpha(\mathbf{x}_1, \ldots, \mathbf{x}_n) = E_\alpha\Psi_\alpha(\mathbf{x}_1, \ldots, \mathbf{x}_n) \ . \tag{2}$$

However, exact solutions to (2) are impractical for systems with large numbers of electrons, and we choose instead to resort to the UHF approximation. One assumes that the many-particle wave function Ψ may be written as

$$\Psi_\alpha(x_1, \ldots, x_n) \approx (n!)^{-1/2}\det|\phi_i^\alpha(x_i)| \ . \tag{3}$$

That is, the solution is approximated by a single Slater determinant of one electron orbitals, ϕ_i^α. In the UHF approximation these orbitals are constrained to be orthonormal and eigenstates of the z component of spin. They are

not constrained to be doubly occupied nor to satisfy precise symmetry restriction. If the orbitals ϕ_i^α are chosen variationally, the Hartree-Fock equation determines the orbitals:

$$F(\rho_i^\alpha)\phi_i^\alpha = \epsilon_i^\alpha \phi^a , \qquad (4)$$

where the density matrix ρ is defined by

$$\rho_\alpha(x,s') = \sum_{i=1}^{n} \phi_i^\alpha(\mathbf{x})\phi_i^{\alpha\dagger}(\mathbf{x'}) , \qquad (5)$$

and

$$F(\rho^\alpha) = -\frac{\hbar^2}{2m}\nabla^2 - \sum_I \frac{e^2 Z_I}{|\mathbf{r}-\mathbf{R}_I'|} + e^2 \int \frac{\rho^\alpha(\mathbf{x'},\mathbf{x'})}{|\mathbf{r}-\mathbf{r'}|} - \frac{e^2\rho^\alpha(\mathbf{x},\mathbf{x'})}{|\mathbf{r}-\mathbf{r'}|} P(\mathbf{x'},\mathbf{x}) . \qquad (6)$$

In Eq. (6), $P(\mathbf{x'},\mathbf{x})$ is the operator which replaces coordinate $\mathbf{x}$ by $\mathbf{x'}$.

For a solid system with low symmetry, such as a solid containing a point defect, solutions to even the UHF system of equations may be difficult if not impossible to obtain in the canonical way.[6] It is therefore useful in such cases to make use of the available arbitrariness in the UHF equation to rotate from solid-spanning Bloch-like orbitals ϕ to solutions localized near particular atoms, if possible. That this may be accomplished has been formally demonstrated by Kunz and Klein,[7] and the theory has been further developed by Kunz.[7] One formally partitions the system into two parts, namely the cluster to be studied and its environment; the latter is assumed known. In the present problem the environment is treated as being the same as the perfect solid. The main effect of the environment for a metal is to act as a source or sink for propagating electrons, and therefore to donate or absorb electrons, as needed, to maintain the Fermi energy of the cluster constant. The cluster has free space as its boundary condition, and the number of electrons is adjusted to keep the Fermi energy constant. Here, all clusters were neutral. Currently, the efforts of several groups are progressing to permit the environment to be treated self-consistently as well.[8]

The UHF method itself omits correlation effects. A brief description of the methods being currently developed and employed to correct this deficiency is needed here. Correlation methods for extended systems are constrained by size-consistency considerations.[9,10] Of the possible methods, our work has chosen those based upon multireference many-body perturbation theory (MR-MBPT). For the present studies, however, only a single reference state is needed at each stage. Nonetheless, here we provide the more general derivation since the single-reference formulation is a special case of the MR-MBPT derivation and the general derivation is no more difficult.

Let the exact Hamiltonian be partitioned into a "simple Hamiltonian," H_0, whose eigenfunctions are known, and a perturbation V:

$$H = H_0 + V . \qquad (7)$$

For our work, we chose H_0 to be the sum of the one-body Fock operators for the n-electron system and we assume we know the determinantal basis sets ϕ and their eigenenergies w:

$$H_0\phi_i = w_i\phi_i .$$

Consider now the first q eigenstates of H_0 separately. The only restriction is that there may be no basis function of H_0 degenerate with the chosen q, unless it is also included in the q. P is a projector onto the space of the q states:

$$P = \sum_{i=1}^{q} |\phi_i\rangle\langle\phi_i| .$$

Consider then

$$H\Psi = E\Psi = (H_0 + V)\Psi ,$$

and assume that we wish to find the many particle state Ψ, for instance. Then,

$$H_0\Psi = (E - V)\Psi$$

and

$$(1-P)(H_0-w_1)\Psi = (1-P)(E-w_1-V)\Psi .$$

Upon commuting $1-P$ with H_0-w_1, we can obtain a formal solution for Ψ, namely

$$P\Psi = \Psi - (H_0-w_1)^{-1}(1-P)(E-w_1-V)\Psi .$$

Now,

$$P\Psi = \sum_{j=1}^{q} \phi_j\langle\phi_j|\Psi\rangle = \sum_{j=1}^{q} \pi_j\phi_j = \Phi, \quad \pi_j = \langle\phi_j|\Psi\rangle ,$$

say, in which Φ is unknown. Nevertheless, one finds

$$\Psi = T\phi , \qquad (8)$$

where

$$T = [1-(H_0-w_1)^{-1}(1-P)(E-w_1-V)]^{-1} . \qquad (9)$$

From this one may obtain the energy from the secular equation

$$(E-w_k)\pi_k = \sum_{j=1}^{q} \pi_j \overline{V}_j , \qquad (10)$$

where

$$\overline{V}_{ij} = \langle\phi_i|VT|\phi_j\rangle . \qquad (11)$$

From a utilitarian point of view, Eqs. (8)–(11) are not complete, in that the unknown energy E occurs in the

denominator of Eq. (9). This will cause difficulties with size consistency[9,10] unless the problem is treated carefully, given that the equations cannot be solved exactly. The difficulty may be circumvented here, as in Rayleigh-Schrödinger perturbation theory, by using the first-order approximation to the energy. To do this, and to solve these equations, one expands the inverse in Eq. (9) in a power series

$$T = 1 + (H_0 - w_1)^{-1}(1-P)(E - w_1 - V) + \cdots$$
$$+ [(H_0 - w_1)^{-1}(1-P)(E - w_1 - V)]^n + \cdots . \quad (12)$$

In this case, the first approximation to E is found by solving

$$(E - w_i)\pi_i = \sum_{k=1}^{q} \pi_k \langle \phi_i \, | \, V \, | \, \phi_k \rangle .$$

If this prescription is followed, and if $q = 1$, for example, one simply recovers ordinary Rayleigh-Schrödinger perturbation theory. The development of MR-MBPT and ordinary MBPT has also been discussed by Bartlett and co-workers.[11]

The techniques employed here can produce highly precise results and spectral properties predicted with great accuracy, when properly implemented. Our calculations were performed upon an FPS-164 scientific computer, which has a 64-bit word length and maintains a precision of 14 decimal digits in computations. Our methods employ expansion of the one-electron orbitals in basic sets of Gaussian-type orbitals (GTO's) contracted to a set of double-zeta accuracy plus polarization functions. All required integrals are evaluated in closed form with these orbitals. We employ a modified polyatom-type approach to the integral evaluations. To simplify storage problems we retain only those two-electron integrals with magnitude greater than 10^{-10} hartrees. The self-consistent-field approximation is implemented by our own UHF code. In this research we require self-consistency in energy to 10^{-6} hartrees and in charge density to 1 part in 10^{10}. Consequently, the computer system and codes must combine to produce a package capable of extremely high precision. Whether or not high accuracy is achieved depends on the choice of basis set and the degree to which the MBPT sequence converges. These several factors are discussed as they arise in the following section. It is worth noting that in the present studies the UHF equations are solved to self-consistency separately for each configuration in question. Therefore electronic relaxation effects and the electron-hole interaction are included directly. Furthermore, because of this self-consistency of each state, Brillouin's theorem is always satisfied. The photon energy required for an optical transition is calculated directly as the energy difference between the two many-electron configurations.

Our work is not the first attempt to use cluster methods or even a UHF cluster approach for solid metallic systems. Extensive early implementations of the cluster method were made by Johnson and Messmer using the scattered-wave $X\alpha$ method.[12] These techniques, while often very illuminating, were aimed at one-electron properties and are not useful for the present study. Alternative

density-functional techniques based on the discrete-variational method, as developed by Ellis and Painter, can be applied to many-electron energies in studies similar to these.[13] The first use of the UHF cluster method for metallic systems was made by Kunz et al. for chemisorption of H by metallic Li,[14] and was later generalized by Marshall et al.[15] Successful extensions to heavy-metal systems were published by Upton and Goddard.[16]

III. RESULTS FOR SUBSTITUTIONAL IMPURITIES IN Li

The research reported here is mainly restricted to divalent substitutional impurities in lithium metal. These impurities include He, Be, Mg, Ca, and Zn. With the exception of He, the impurities all exhibit similar theoretical behavior in the Li-metal host. As it includes both ground and excited states, this study represents a substantial number of calculations, and, in the interest of economy, it was necessary to keep both the basis set and cluster size to a minimum. Previous studies of Li clusters by Marhsall, Blint, and Kunz show that a nine-atom bcc cluster of Li has the same charge density near the central atom as that obtained by energy-band theory.[15] Therefore, in this work we normally used a cluster consisting of the central atom and two shells of neighbors, comprising 15 atoms in all. For a few examples we extended the cluster to include third and fourth neighbors, but found that this makes little significant difference to the spectroscopic properties of the impurities, with changes in transition energy of less than 0.1 eV.

The basis-set choice is a more significant problem. For magnesium atoms, for example, we used a set of five s orbitals and three p orbitals, with each orbital a superposition of several primitive Gaussians. Other systems were proportionately sized. These sets were optimized to provide good self-consistent-field (SCF) descriptions of the free atoms and reasonable correlation descriptions of the solid system. Such small sets are not optimal for correlating the free atoms owing to limitations in the angular basis of the set. The problems are less significant in the solid because basis functions on the atoms surrounding a given atom simulate the required higher-angular-momentum states quite well. These basis sets are therefore useful in a solid, but less so for the free atom. We have performed spectroscopic studies with the same basis sets for the free He, Be, Li, and Mg atoms. The worst comparison with experiment by far is for the Mg atom. It will be used as a test in the example case outlined below.

Finally, the convergence of the MBPT method warrants discussion. Bartlett and co-workers[11] find that, in second order, about 90% of the correlation energy contained in a basis set is obtained, and about 95% in fourth order. For chemical accuracy one typically needs fourth-order corrections. For our purposes of solid-state spectroscopy, however, an accuracy of 0.1 eV is more than enough. This is much less restrictive than chemical accuracy (~ 0.01 eV), and from the UHF starting point, second-order perturbation corrections then suffice. We have run a number of tests using third-order or third- and fourth-order MBPT, or even fourth-order MBPT plus partial

sums of convenient terms to infinite order, and find that none affect the spectroscopic energies by as much as 0.1 eV. Therefore, we use second-order perturbation theory for the present research. The conclusions agree with recent studies by Beck and Kunz.[17]

The Mg atom. To test the methods used here, a series of atomic calculations were performed, including the Mg atom. The lowest excitation of the free Mg atom is $3s^2 \rightarrow 3s\,3p$. This is a transition from $^1S_0$ to either the $^3P_1$ or $^1P_1$ excited configuration. The $^3P_1$ state is observed experimentally to lie 2.7 eV above the ground state, and the $^1P_1$ state lies 4.3 eV above the ground state. In our UHF calculations the $^3P_1$ state is found to lie only 2.0 eV above the ground state. We have also computed the UHF "singlet-excited-state" energy. In fact, this state contains a significant $^3P_1$ admixture. In a minimal configuration interaction (CI) to recover a pure singlet state, the UHF $^1P_1$ lies 4.9 eV above the ground state. In all cases reported in this paper, we perform such a minimal CI to recover the singlet state, in accordance with the MR-MBPT formalism given in the preceding section. Neither the absolute accuracy nor the multiplet splitting is in good agreement with experiment. When we recompute these levels using second-order MBPT, however, the $^1P_1$ state shifts to 4.0 eV and the $^3P_1$ state falls at 2.4 eV. Even with the relatively poor basis set, these results evidently give fair agreement with experiment for absolute energy (4.3 and 2.7 eV) and are in excellent agreement with observed values of the multiplet splitting. We shall see that the effect of correlation on spectral energies is not usually so dramatic and the shifts are, in general, much smaller in the solid than in the free Mg atom.

Divalent impurities in Li metal. Similar methods were employed in calculations for impurities in Li metal. For He, Be, and Mg, where the impurities are similar in size to Li or smaller, the Li atoms were held in their perfect-lattice position. For Ca and Zn, where the impurity ions are greater in size than Li, the nearest-neighbor Li atoms were relaxed outward to the Li-atom—impurity distance obtained by energy minimization. Mg excitations in Li have the transition to the $^1P_1$ level red-shifted to 2.67 eV in the UHF approximation and to 2.76 eV with second-order correlation. This is in good agreement with the value of 2.8 eV found experimentally.[1] A significant quenching of the correlation shift evidently occurs in the solid host. This is probably because the conduction electrons screen the interaction between the excited Mg $3p$ electron and the Mg ion, thereby reducing the host correlations while inducing solid-state ones instead. These are apparently well represented on the average by the ΔSCF UHF procedure.

That this excitation is well localized is clear from Fig. 2, which shows the charge-density contours for the (110) cut through the cluster. Figure 2(a) shows the Mg ground state and Fig. 2(b) shows its excited state. The excitation causes a distortion which is almost entirely confined to the central cell.

In our calculations we have also investigated the electronic structure when a Mg atom has a Mg atom as one of its nearest neighbors, the remainder being Li atoms. On the average, this corresponds to an alloy of about 12 at. %
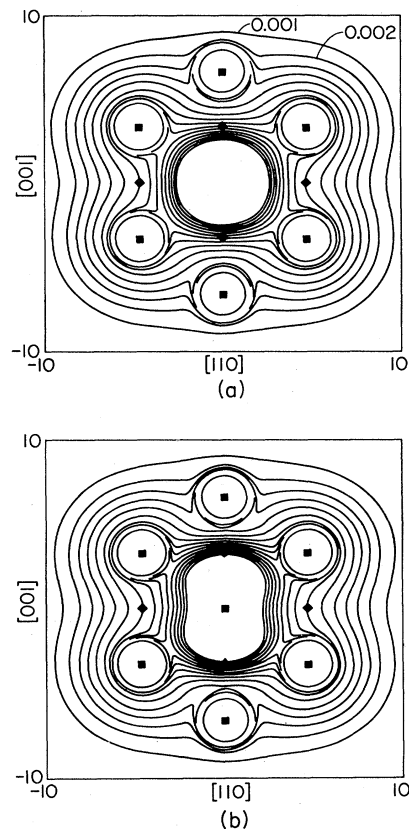

FIG. 2. Panel (a) shows charge-density contours for the Li-Mg cluster in its ground state (distances in bohrs). The chosen (110) plane of bcc Li metal includes the central Mg atom. Panel (b) shows the same cluster with the central Mg atom excited. Squares mark the seven atoms in the central plane of the 17-atom cluster, and diamonds indicate the four atoms in the (110) planes above and below it. The only atoms in the next planes overlap the central atom. Densities are in electrons/bohrs.[3] Contours are omitted in the atomic cores, where they become inconveniently numerous.

Mg concentration. The excitation energy is red-shifted by about 0.2 eV from that of the isolated Mg impurity. Evidently, the two Mg impurities interact only weakly, as one might have anticipated from the localization of the contour changes seen in Fig. 2. The contour map of charge density for the impurity pair excitation is shown in Fig. 3(a). Figure 3(b) shows schematically the one-electron energy levels of the Mg atom.

Next consider the analogous calculations for Zn and Zn_2 in Li metal. The Zn-impurity structure in Li metal was computed for both the ground $4s^2$ and the excited $4s\,4p$ configurations. The UHF energy with second-order correlation correction gives the theoretical first optically excited state at 2.48 eV. This compares quite well with the experimental value of 2.6 eV reported in paper I.[1] Charge-density plots for the ground and excited configurations of the Zn impurity are shown in Fig. 4. They indicate that the excited Zn is still quite well localized, but is nevertheless noticeably more extended than the excited
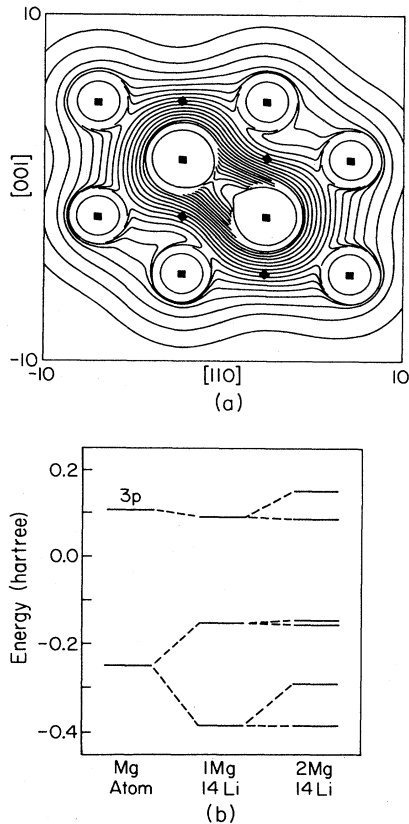
(a)

(b)

FIG. 3. In panel (a) ground-state charge-density contours are shown for a cluster with two nearest-neighbor Mg atoms in Li metal. A (110) cut is again used. A small symmetry breaking has appeared in the UHF calculation. Panel (b) shows the evolution of one-electron eigenvalues for Mg, Mg in Li metal, and Mg_2 in Li metal, with energies in atomic units of $e^2/a_0 = 27.2$ eV (Ry). In the solid the lower levels are for bandlike states, and the upper levels are for states which participate in the local excitation. Note how weakly the two local states interact for Mg_2.

Mg, as is evident from a comparison of Figs. 2(b) and 4(b). The lesser localization is further confirmed by the energy splittings when Zn has one Zn nearest neighbor. The excited orbitals apparently interact significantly, as seen in Fig. 4(c). This level splitting could cause the concentration-dependent broadening observed experimentally. It may also account for the disappearance of the absorption peak at Zn concentrations of about 10 at. %.

Pure Mg metal. Before concluding this section we comment on a related phenomenon which is of considerable interest. It is reported in paper I that the Mg $3s^2 \rightarrow 3s\,3p$ resonance in Li metal can be followed across the entire Mg-Li phase diagram, even to the limit of pure Mg metal. In pure Mg metal the resonance becomes the feature which has, in the past, been identified as the Mg interband transition.[18] This is an extraordinary correlation. The resonance maintains approximately a constant oscillator strength *per Mg atom* and is not significantly perturbed by the bcc-to-hcp transition that these alloys undergo with increasing Mg content. One may deduce
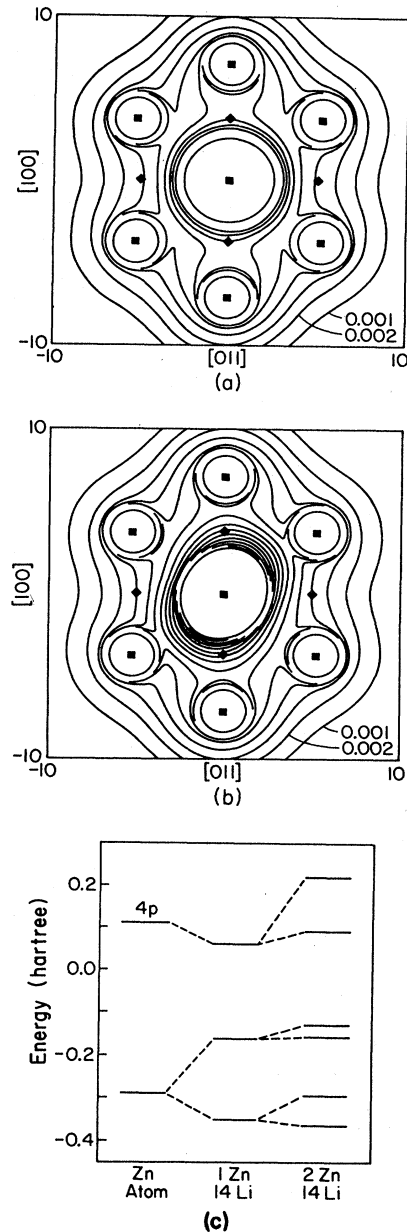

(a)

(b)

(c)

FIG. 4. Ground-state charge density contours for Zn impurities in Li metal on a (110) cut are given in panel (a). Panel (b) shows the excited-state charge density for Zn impurities in Li metal. This is less local than Mg in Li [Fig. 2(b)]. Enhanced level splittings for Zn-Zn pairs are seen in panel (c) as a consequence of the delocalization.

that the phenomena depend on the electronic structure near each Mg atom in the alloy and are insensitive to fine details of the band structure. A possible explanation involves the local electron-hole—interaction process considered in this paper. The question to be answered is whether or not the theory confirms that this process can give rise to the resonance in pure Mg metal, in addition to its successful account of the Li-rich regime described above.

An earlier effort to treat these effects has been reported by Kunz and Flynn.[19] These authors employ a superposition of the vertical electron-hole—pair band excitations of one-electron theory to obtain true many-body excited states of the interacting system. They find that the electron-hole interaction causes oscillator strength near the interband edge to be strongly enhanced. This happens because the electron-hole overlap is increased for low-lying excited states and suppressed for higher excitations. For reasonable values of the electron-hole interaction, the optical spectrum is reproduced rather well.

A detailed insight into the electronic excited configuration near the band edge may be obtained from explicit calculations of electronic structure on small systems. Therefore it appeared of particular interest to apply the cluster methods described above to the electronic excitations of pure Mg metal.

The case of Mg metal has therefore been investigated using UHF theory plus MBPT for systems of 1 Mg atom, 7 Mg atoms, 13 Mg atoms, and 19 Mg atoms. The basic set employed in these studies was identical to that used for the treatment of Mg in Li described above. As indicated there, the atomic transition $3s^2(^1S_0)$ to $3s\,3p\,(^1P_1)$ lies at 4.0 eV. With the first plane of Mg neighbors present (seven-atom cluster), this transition falls in energy to 2.2 eV, and finally to about 1.2 eV for the 19-atom three-dimensional cluster. This is *not*, however, the first-excited state of the cluster. Instead, it is the excitation for which the s hole and the p electron retain maximal atomiclike (local) character. The calculations placed the excitation on the central cell of the cluster, where it remained with an electron density resembling that of excited Mg in Li, but somewhat less localized. Electron-density contours for the ground and excited configurations are given in Fig. 5. Similar states centered on neighboring Mg atoms, together with the hopping matrix elements among the sites, must spread the pair excitations into a resonance of optically active, highly correlated, but delocalized electron-hole—pair states, much as in the theory of Kunz and Flynn. For the 19-atom cluster, the excitation onset lies at 0.6 eV, but there is little localization of valence hole and conduction electron in this lowest configuration. In all, the case of Mg in Mg metal resembles Mg in Li metal fairly closely, but the electron-hole resonance is not quite as localized as in the Li-metal host lattice.

In summary of the results reported in this section, it may be noted that the procedures employed here appear to provide an accurate and useful description of the ground and excited configurations of metal clusters. Excitation energies may be calculated to the order of 0.1 eV. The explicit wave functions allow a detailed insight into the spatial form of the electronic structure. This has been particularly valuable in revealing the tight localization of the carrier pair excitations, almost within a single cell of the lattice. The methods provide an effective way to use advanced computational capabilities for the solution of solid-state problems.

IV. EFFECT OF CORE STRUCTURE ON EXCITATION ENERGY

The divalent impurities Mg, Zn, and Ca have very similar excitation energies in Li metal,[1] and also possess simi-
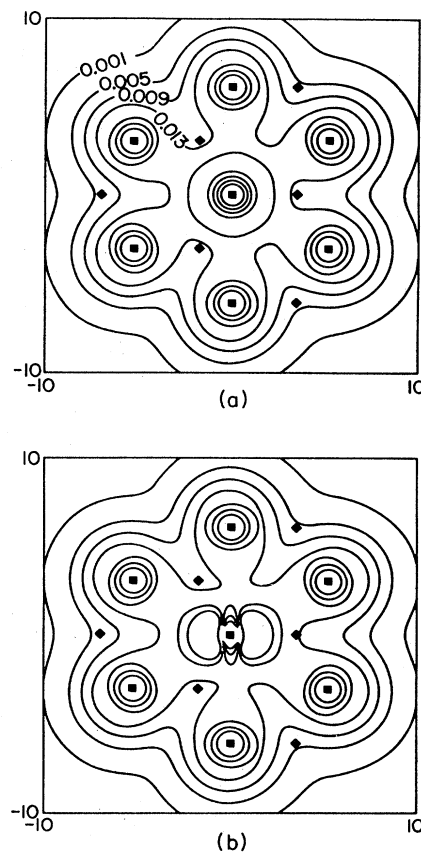

FIG. 5. Electron-density contours for the localized $3s\,3p$ configuration in pure Mg metal. The cluster consists of three successive close-packed planes of the hcp lattice with seven atoms in the central plane (squares) and six atoms in the two outer planes (diamonds). Panel (a) shows the electron density in the ground state in the central plane, and panel (b) shows the excited configuration. Just as for Mg impurities in Li metal (Fig. 2), the excited electron and hole can localize tightly on one Mg atom. Note that the contour density intervals (in electrons/bohrs^3) differ from those of Figs. 2—4.

lar widths. In this section we discuss these facts and offer some semiquantitative interpretation.

Results calculated by means of the theoretical model described in Sec. III are collected in Table I. The Ca and Zn $4s$ orbitals differ by more than 1 eV in the atom, but this difference does not appear in the band bottom or local one-electron energies in the clusters. For Mg $3s$ orbitals the theory gives much the same result. Only for the smaller ions, Be and He, does a tendency towards formation of local bound states occur. For the Be-Li cluster the band bottom and local states become strongly admixed, while for He in Li metal the local state leaves the band bottom and falls below the atomic value.

It appears likely that two factors contribute to this behavior. First, it has been known since the work of Friedel[20] and Slater[21] that resonant impurity levels in a band change energy relatively slowly with an increasingly attractive local perturbing potential, and finally emerge

TABLE I. Impurity one-electron energy levels in Li metal (in Ry).

Impurity	State	Atomic level	Band bottom	Local state
He	$1s$	−0.92		−1.00
Be	$2s$	−0.30	−0.50	−0.239
Mg	$3s$	−0.253	−0.384	−0.153
Zn	$4s$	−0.287	−0.352	−0.160
Ca	$4s$	−0.195	−0.353	−0.153

quickly from the band bottom. Explicit Green's-function calculations for Mg in Li metal by Inglesfield[4] have shown very clearly the accumulation of s^2 density near the band bottom caused by this. Presumably, the similarities among the s^2 levels of Mg, Zn, and Ca arise largely from this stabilization. One-electron effects of the same type can be followed directly by using a simplified one-band Coster-Slater[21] model with an increasingly attractive single-site perturbation.[22]

The second factor relevant to the rapid emergence of the s levels from the band bottom is metallic screening. The "screening length" for Li is about 0.8 Å, which is significantly less than the orbital radii, ~ 2 Å, of Mg, Zn, and Ca. This is not the case for Be (1.3 Å) and He (1.2 Å). For these latter impurities, the conduction electrons are not so effective in weakening the impurity field by screening, and the impurity is able to bind the outer s^2 levels more deeply.

V. CONCLUSIONS

The purpose of this paper is to present a theoretical model which can describe local impurity excitations in metals. Of particular interest are methods which are able to deal with localization of the electron and hole through their mutual interaction in the metallic environment. A second requirement is the ability to predict excitation energies with an accuracy of ~ 0.1 eV comparable with that of the experiments.

The treatment described in this paper combines the unrestricted−Hartree-Fock method with correlation corrections introduced by means of multireference many-body perturbation theory. These procedures are applied to small clusters of metal atoms to provide completely a priori calculations of the total energy and electronic structure, not only of the ground configuration but of electronically excited configurations also. When optimally programmed, the calculations remain computationally intensive, but quite feasible on a fast computer. In the present work about 100 h of FPS 164 time were required for the UHF clusters and about 100 h for MBPT correlation corrections.

Given that the methods converge, the merits of the theory may best be judged from the fidelity with which the results describe experimental observations. The tests reported above for atoms focus on a difficult case for the theory, but one which is directly relevant to the experiments on metals. The theory is found to predict the atomic excitation energies of divalent atoms with errors of

a few tenths of 1 eV, and their multiplet splittings to about one-tenth of an electron volt. Given the limited angular flexibility of the basis set, this is highly satisfactory. The results for clusters are expected to be better because the variety of orbitals is greater.

The convergence of the procedures themselves warrants additional brief comment. For metallic particles of the type investigated here, the degree to which properties achieve size independence depends strongly on the particular property studied. Those properties which intrinsically require information about the entire system may change markedly with the size of the system. As mentioned above, for example, the excitation gap of Mg clusters varies very considerably with cluster size. On the other hand, it is shown in earlier work[15] that the electron density near the central cell is quite insensitive to cluster size, and in unpublished work we have shown that the work function exhibits a similar insensitivity. In the present research we have shown that the localized excitations of a central atom are equally independent of cluster size, even for very small systems. Energy shifts of < 0.1 eV take place as shells are added beyond the first two sets of neighbors, and this is less than the uncertainties inherent in the model. We therefore feel that this model can be extremely useful for the type of calculation described here.

We have reported the application of these methods to certain excitations in alloys and pure metals. In doing so it was our hope to explain the energy and strength of the $ns^2 \rightarrow nsnp$ excitations exhibited by divalent impurities in Li. The effects of impurity concentration on the excitations were also of interest. This is especially the case for the Mg-Li system, where the resonance is observed across the entire phase diagram from the dilute limit to pure Mg, where it becomes the interband edge. In this application our calculations reproduce the observed excitation energies within the experimental uncertainties, not only for divalent ions at dilution in Li, but also for the interband transition of pure Mg metal. In each case the explicit wave functions show that the excited electron and hole localize together rather tightly, being confined mostly within one atomic cell. This localization confirms the experimental inference and, at the same time, justifies the use of small clusters since an optically active region does not overlap the boundary of the crystal. Furthermore, there is an indication that the overlap of excitations at defect pairs may offer an explanation of the variation of excitation profile with concentration in the dilute limit. This aspect of the results remains less well developed at the present time, and further work will be required to elucidate the behavior more completely. Regardless of this, however, it is clear that a reliable theoretical procedure for modeling electronic excitations in alloys is now available. We expect that these methods will quickly find application to numerous problems in which many-body effects play an important role in metals and alloys.

We return finally to the experiments which prompted the present application of the theory. As mentioned above and in paper I, these point very directly to a breakdown of the one-electron description of optical processes in metals. There is no doubt that the theoretical results reported in

Sec. III lend very strong support to the experimental claims. There is indeed a large degree of electron-hole localization for excitation energies which are in accord with the observations. This localization ensures that the excitation is the dominant optical process. The theory confirms that this can happen in the interband transition, even in a translationally invariant metal such as Mg, where one-electron theory affords no mechanism whatsoever for localization.

A number of phenomena remain for future explanation. For example, the question of impurity-impurity—interaction effects in the optical spectrum requires further understanding. Cluster methods are not well suited to a discussion of quasiparticle excitations, as the energy spacing of band orbitals is often too large. As a consequence, we have not been able to discuss excitation line shapes in this report. In this respect the continuum theory of Kunz and Flynn is more useful at present. Finally, it remains to ask how widespread the effects of the electron-hole interaction on the optical spectrum are. Are these processes restricted to a few odd cases involving divalent ions, or are they instead more widespread? In calculations to be published elsewhere, we have found that the electron-hole coupling has only a weak influence on the conduction-band excitation spectra of pure alkali metals. It cannot be doubted, however, that transition-metal ions involve precisely those phenomena for d-level excitations that the divalent ions bring about for s-level excitations. For this reason it is our expectation that the effects are rather widespread in alloy spectra, and that the breakdown of single-particle theories for the optical properties of metals and alloys is a frequent occurrence which must become widely recognized.

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