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Relativistic effects in mercury: Atom, clusters, and bulk

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We study the effects of relativity on the electronic structure of Hg as it evolves from an atom to a cluster, and then to the bulk. A comparison of nonrelativistic and scalar-relativistic results for bulk Hg, obtained self-consistently, clearly shows the importance of including the relativistic terms as well as treating the $5d$-electrons as valencelike. Our cluster calculations show that the relativistic effects are equally important for clusters, and that the differences in many electronic properties such as the size dependence of the gap energy and the l character of Hg clusters with respect to other divalent-metal clusters, for example, Be and Mg, arise due to the relativistic terms, thus providing further insight into the electronic origins of these properties.

I. INTRODUCTION

The changes in the electronic properties of atomic clusters of divalent-metal atoms as they evolve from atoms to clusters, and then to bulklike systems, continues to be intensely investigated both experimentally[1] and theoretically.[2–6] In general, it is found that very small clusters of the divalent-metal atoms such as Be, Mg, Hg, etc., are insulating, while larger clusters exhibit continuous evolution toward metallic bulklike behavior.

Although atomic Hg has a closed s-shell configuration ($5d^{10}6s^2$) similar to Be and Mg, a theoretical understanding of the electronic properties of Hg clusters, Hg_n, or bulk is much more difficult than that of Be_n and Mg_n because of the high atomic number of Hg and the presence of $5d$ electrons close to the $6s$ level. The high atomic number of Hg underscores the importance of relativistic effects in determining its electronic structure while the closeness of $5d$ electrons to the $6s$ level indicates the possibility of non-negligible s-d hybridization. The relativistic effects on the electronic structure of atomic Hg are well documented,[7] whereas previous theoretical studies[8] of these effects on the band-structure of bulk Hg are based on (i) non-self-consistent charge densities, and (ii) the treatment of $5d$ electrons as core electrons. For Hg_n, *ab initio* studies[4] on neutral and charged dimers have been carried out using the pseudopotential and the configuration-interaction methods. But, it appears that there has been no systematic study of relativistic effects on Hg_n, although such a study can provide a better understanding of the electronic properties of these clusters. In addition, it is quite possible that some of the differences in the electronic properties of Hg_n *vis-à-vis* Be_n and Mg_n may have a relativistic origin. Also, the electronic structure calculations based on approximations (i) and (ii) are in general not very reliable, and as such *empirical* tight-binding cluster calculations[5] that use these results for parametrization cannot be expected to describe accurately the electronic structure of Hg_n. The present study was motivated by the concerns outlined above, and is intended to be the first step towards improving our understanding of the electronic properties of Hg as it evolves from an atom to a cluster, and then to the bulk.

In this paper we examine the effects of including the relativistic terms, the so-called mass-velocity and Darwin terms, on the electronic structure of both bulk and clusters of Hg by carrying out charge self-consistent bulk calculations using the linear muffin-tin orbital (LMTO) method[9,10] in the atomic-sphere approximation (ASA) with the nonrelativistic Schrödinger equation as well as with the scalar-relativistic Dirac equation. Our calculations consider $5d$ electrons to be valencelike and thus allow $5d$ bands to hybridize with the $6s-6p$ bands. For examining the relativistic effects on Hg_n, we use an approach,[11] outlined below, that is based on the tight-binding formulation[10] of the LMTO method, and it offers the possibility of being developed into a reliable and very efficient *ab initio* electronic structure method in real-space for $n \geq 20$, in contrast to the conventional *ab initio* methods[4,12] which become computer-intensive for $n > 20$.

Based on our calculations, we find that the mass-velocity and Darwin terms (i) significantly increase the s-p "level" separation in the bulk, thereby reducing the s-p hybridization, and (ii) move the lower s-band edge below the bottom of the d band, resulting in increased s-d mixing. In contrast to assumptions implicit in earlier calculations,[8] we find strong evidence for treating $5d$ electrons as valencelike. Our cluster calculations show that the relativistic effects are very important for an accurate electronic structure description of Hg_n, and that the differences in many electronic properties of Hg_n with respect to other divalent-metal clusters such as Be_n and Mg_n arise mainly from the mass-velocity and Darwin shifts, which provide further insight into the electronic origins of these properties. For example, we find that the size dependence of the gap energy and the l character of the nonrelativistic Hg_n are very similar to that of Mg_n. Before discussing the results we outline the procedure followed for calculating the electronic structure of bulk and clusters of Hg.

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II. RESULTS AND DISCUSSION

The nonrelativistic (NR) and the scalar-relativistic (SR) self-consistent electronic structure of bulk Hg is calculated with the LMTO method, assuming a face-centered-cubic (fcc) lattice structure. The exchange-correlation potential is parametrized as suggested by von Barth and Hedin. The nonspherical charge density of bulk Hg is calculated as described in Ref. 13. The SR results for fcc Mg, used in the following for comparison with Hg, are obtained similarly. Note that for suppressing the uncertainty involved in comparing the results of different lattice structures, we use fcc lattice structures for both Hg and Mg although their equilibrium crystal structures correspond to rhombohedral[8] and hexagonal close-packed, respectively.

For the cluster calculations we use the Löwdin orthonormalized LMTO Hamiltonian,[10] $\mathbf{H}^{(2)}$, expressed in terms of the tight-binding first-order Hamiltonian, $\mathbf{h}^{\beta}$,

$$\begin{aligned}\mathbf{H}^{(2)} &= \mathbf{E}_{\nu} + \mathbf{h}^{\beta}(1+\mathbf{o}^{\beta}\mathbf{h}^{\beta})^{-1}\\ &= \mathbf{E}_{\nu} + \mathbf{h}^{\beta} - \mathbf{h}^{\beta}\mathbf{o}^{\beta}\mathbf{h}^{\beta} + \cdots ,\end{aligned} \tag{1}$$

where bold-faced symbols are matrices in site and angular momentum indices, β's are the screening parameters, and the diagonal matrices $\mathbf{E}_{\nu}$ and $\mathbf{o}^{\beta}$ are the potential parameters determined self-consistently from the electronic structure calculations of bulk Hg. In our calculations we effectively sum the right hand side of Eq. (1) until convergence is achieved for each cluster. Further details about our approach, including the effects of keeping different terms in the expansion for $\mathbf{H}^{(2)}$, will be published elsewhere.[11]

The electronic structure of NR and SR Hg$_n$ with n ranging from 2 to 79 is calculated by the exact diagonalization of the cluster Hamiltonian, Eq. (1), although for larger clusters use of the recursion method is computationally much more efficient.[6] The atomic arrangement of clusters for $n \geq 13$ corresponds to fcc shell closures at 13, 19, 43, 55, and 79 atoms, respectively, and for $n = 5$ we used a planar fcc-like geometry. For $n < 19$ the present approach can be considered as a parametrization, with hopping parameters reproducing accurately the electronic structure of bulk Hg. For $n \geq 19$, as stated earlier, our approach can form the basis for *ab initio* calculations in real-space. The Fermi energy of each cluster is determined by adding a Lorentzian of full-width 0.05 eV to the states close to the Fermi energy.

Here we would like to point out that within the approach followed in this paper there are a number of ways by which the electronic structure description of Hg, bulk or clusters, can be improved. Some of them are (i) use of a no-shape approximation for the potential instead of the spherically symmetric potential used in the ASA, (ii) the inclusion of spin-orbit terms, especially for cluster calculations where spin-orbit splitting of the d level has important consequences,[5] (iii) charge self-consistency and structural optimization for clusters, (iv) inclusion of improved parametrization of the correlation effects for smaller clusters, and (v) use of site-dependent screened structure constants for cluster calculations. These improvements are expected to be significant, especially for smaller clusters.[14] However, the main purpose of this paper is to examine the effects of relativity, which are found to be very *robust* for both bulk and clusters of Hg, and hence we do not expect qualitative changes in our results due to these improvements.

A. Atomic and bulk Hg

In Table I we compare the calculated equilibrium lattice constant, the cohesive energy, and the bulk modulus of Hg with the experimental values. The results of the SR calculations are much closer to the experimental values than are the results of NR calculations. The decrease in the SR lattice constant of about 1% with respect to the NR lattice constant is due to the contraction of the s-wave function.

Since the effect of relativistic terms on a Hg atom is a precursor of its effect on bulk Hg, in Fig. 1(a) we show the changes in the potential parameter C_l, defined to be the center of the l band,[10] due to relativistic terms obtained from bulk-Hg calculations with the lattice constant a = 20 a.u., which essentially corresponds to free-atom results (the total energies are within 0.03 mRy of the free-atom total energies). As expected, the s level becomes deeper and the d level moves towards the s level. Consequently, the s-d level separation $E^{\mathrm{atom}}_{s\text{-}d}$, is decreased from 0.49 Ry to 0.22 Ry, while $E^{\mathrm{atom}}_{s\text{-}p}$ is increased from 0.45 Ry to 0.69 Ry. Some of the differences between our results and that of Ref. 7 are due to the different exchange-correlation potential used in our calculations. Based on the effects that the relativistic terms have on the atomic Hg, one can imagine that in the case of bulk Hg these effects will lead to increased s-d mixing and reduced s-p hybridization. Indeed this is the case for bulk Hg, as can be seen from Fig. 1(b), where we show the C_l values for both NR and SR bulk Hg calculated at their respective equilibrium lattice constants. It shows significant change in $E^{\mathrm{bulk}}_{s\text{-}d}$ and a substantial increase in $E^{\mathrm{bulk}}_{s\text{-}p}$ due to relativistic terms.

The movement of the band center C_l due to relativity leads to profound changes in the densities of states, as shown in Fig. 2, where we plot the l-decomposed densities of states for both NR and SR bulk Hg calculated at their respective equilibrium lattice constants. The substantial bandwidth of 5d electrons, clearly evident in Fig. 2, justifies the need for treating them as valence electrons. A comparison of Figs. 2(a) and 2(b) reveals that the center of the d band has moved closer to the Fermi energy and the d-band width has increased due to relativity, although there is an overall narrowing of s and p

TABLE I. Calculated equilibrium lattice constants a, cohesive energy E_{coh}, and the bulk modulus B, and the corresponding experimental values for bulk Hg.

	NR	SR	Expt.
a (a.u.)	8.659	8.563	
E_{coh} (eV/atom)	1.607	0.787	0.67
B (Mbar)	0.698	0.442	0.382

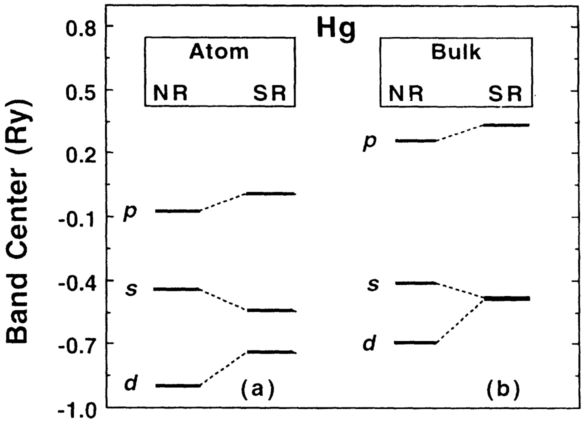

FIG. 1. The NR and SR band center C_l for (a) a Hg atom and (b) bulk Hg. The energy in (a) is measured with respect to the electrostatic potential at the Wigner-Seitz sphere-boundary, while in (b) it is measured with respect to the Fermi energy.

bands. In the SR case, Fig. 2(b), the bottom of the s band has moved below the d band, leading to significant s-d hybridization, and thereby increasing the number of s electrons from 0.934 in the NR bulk Hg to 1.327.

To underscore the importance of 5d electrons in determining the electronic structure of Hg, we show in Fig. 3(a) the SR nonspherical valence charge density of bulk Hg. The corresponding NR nonspherical valence charge density is very similar to that of Fig. 3(a) except well inside the Wigner-Seitz radius. The expected changes in the outer region due to the contraction of the s-wave function are swamped by the changes in the d-electron charge density. For comparison with other divalent-metals, in Fig. 3(b) we show the SR nonspherical valence charge density of bulk Mg calculated similarly. In Mg the s-p hybridization leads to covalentlike charge distribution, as evidenced by the accumulation of charge along the nearest-neighbor directions in Fig. 3(b). This is not the case for either NR or SR nonspherical valence charge density of bulk Hg, which ensures that the detailed electronic response of Hg would be quite different from that of Mg.

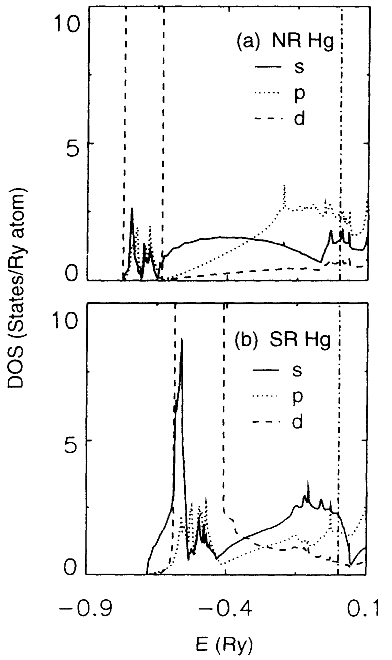

FIG. 2. The l-decomposed densities of states for fcc Hg calculated (a) nonrelativistically and (b) scalar-relativistically. The Fermi energy is denoted by the dot-dashed line.

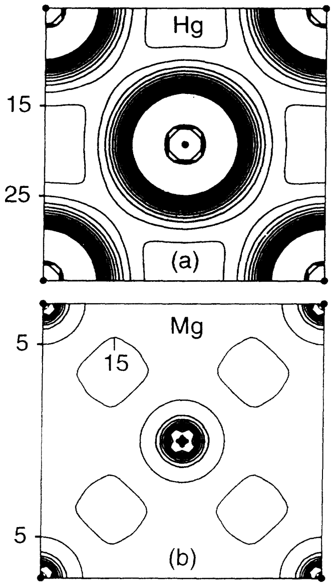

FIG. 3. The valence charge densities of (a) Hg and (b) Mg in the (001) plane of the fcc lattice calculated scalar-relativistically. The filled circles denote Hg (Mg) atoms in (a) [(b)]. The contours are plotted at an interval of 10 in units of 10^{-3} electrons/(a.u.)^3.

B. Clusters of Hg

So far we have discussed the effects of the relativistic terms on the electronic properties of bulk Hg. To see if the relativistic terms can perceptibly change the electronic properties of Hg_n, we examine the size dependence of the total densities of states (DOS), the gap energy, Δ_n, and the l character of NR and SR Hg_n.

In Fig. 4 we compare the total DOS for Hg_{79} with that of bulk Hg for both NR and SR cases. It clearly shows the importance of including the relativistic terms as well as of treating 5d electrons as valencelike. For other cluster sizes the relativistic effects on the densities of states are similar. The downward movement of the NR total DOS in Fig. 4(a) is not entirely due to size effects, but is partly because of (i) the uncertainty in determining accurately the Fermi energy when extended s and p states are involved, and (ii) the imposition of self-consistency on the cluster Hamiltonian of Eq. (1).

To examine the size dependence of Δ_n as well as to illustrate the effects of relativistic terms, we show in Fig.

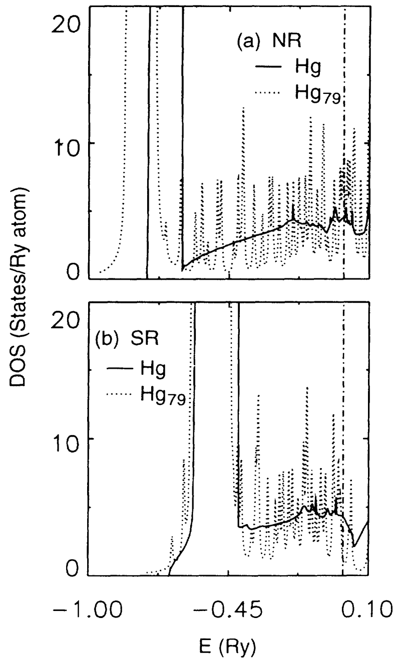

FIG. 4. The total densities of states for Hg_{79} calculated (a) nonrelativistically and (b) scalar relativistically. For comparison the total density of states for bulk Hg is also shown. The Fermi energy is denoted by the dot-dashed line.

5 the variation of Δ_n with n for NR and SR Hg_n. In the same plot we also show the n dependence of the gap energy for Mg_n. For SR Hg_n our calculations of the size dependence of Δ_n agree quite well with the results of other calculations.[5,6] Because the NR $E^{\text{bulk}}_{s-|p}$ is smaller than the corresponding SR separation, and is comparable to the level separation in Mg, we expect NR Hg_n to behave more like Mg_n than SR Hg_n. Not surprisingly, the size dependence of Δ_n for NR Hg_n is almost identical to that of Mg_n, as can be seen from Fig. 5. The NR Δ_n for Hg_n essentially vanishes around $n \approx 13$, whereas the SR Δ_n is still quite large for $n \approx 13$, and it goes to zero around $n \geq 80$, indicating clearly that the differences in the size dependence of the gap energy between Hg_n and other divalent-metal-atom clusters such as Be_n and Mg_n arise due to relativity.

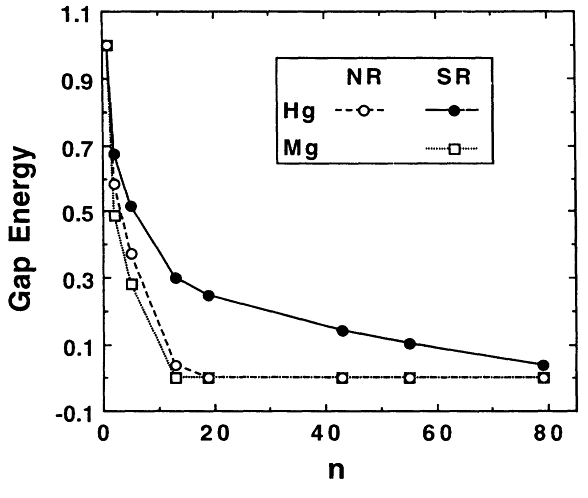

FIG. 5. Variation of gap energy Δ_n for NR Hg_n and SR Hg_n and Mg_n. Note that Δ_n's are normalized by their respective Δ_1's in each case.

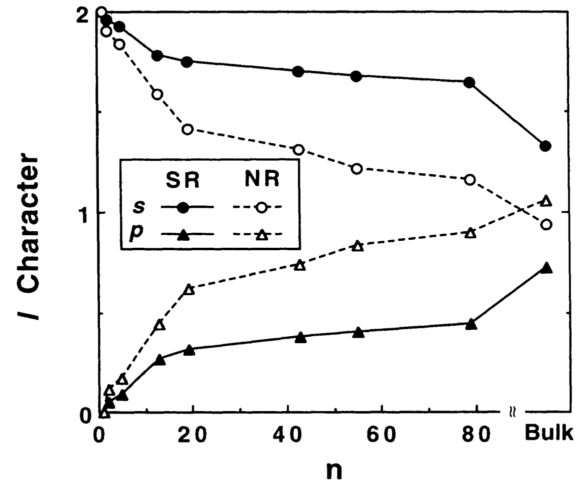

FIG. 6. The l character for NR and SR Hg_n as a function of cluster size. The number of s and p electrons for bulk Hg is also shown.

Another example, where relativity changes the electronic properties of Hg_n, is provided by the variation of the l character with n. In Fig. 6 we show the s and p characters of NR and SR Hg_n. The variation in the d character, not shown in the figure, is small. Starting with two s electrons for Hg atom, the evolution towards bulklike l characters depends significantly on the relativistic terms. The increased s-p level separation in the SR case effectively suppresses the s-p hybridization, and thus reducing the number of p-like electrons for increasing cluster sizes. Once again, the variation of NR l character is very similar to that of Mg_n.

III. CONCLUSIONS

We have shown that for an accurate electronic structure description of bulk Hg one must include the relativistic terms, and treat the $5d$ electrons as valence electrons. From our cluster calculations we have demonstrated that the relativistic effects are equally important for clusters of Hg, and that the differences in many electronic properties such as the size dependence of the gap energy and the l character of Hg_n with respect to other divalent-metal clusters, especially Mg_n, arise due to relativity.

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