

Tight-binding Calculation of Size Dependence of the Ionisation Potentials of Mercury Clusters

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Abstract

The gradual transition from van der Waals-like to metallic behaviour in mercury clusters is studied by a localised orbital theory based on the tight-binding approximation. The total density of states (DOS) of the Hg_n clusters is obtained by means of the moment expansion method. The Fermi energy determined from the DOS is combined with the classical conducting sphere droplet (CSD) model to calculate the size-dependent ionisation potential (IP) of the cluster. The theoretical results are in good agreement with the experiments. The size dependence of the ionisation potential has an abrupt change at $n = 13$, indicating that the transition from insulating to metallic behaviour begins.

1. Introduction

The physical and chemical properties of metal clusters have received considerable attention during the last decade (Morse 1986; Moskovits 1991). It is of fundamental interest to know how the discrete electronic states in the cluster are broadened to form the band structure of the bulk solid and the metallic properties of the clusters evolve as a function of cluster size. Particularly interesting in this respect are the divalent metals, which have an s^2 closed-shell atomic configuration just like helium, and should in principle be insulating in the bulk. In fact, the binding energy of these metals in homonuclear dimers is so weak that these dimers quite often are considered analogues of the weakly bound rare gas dimers (Morse 1986). But it is well known that the bulk solid of these elements has a metallic character resulting from the overlap between the filled s band and empty p band. Although the dimers and other smaller clusters are generally van der Waals-like, metallic cohesion must eventually prevail in the larger aggregates. Therefore, probing the transition from van der Waals to metallic bonding in divalent metal clusters has become one of the foci in cluster research (Rademann *et al.* 1987; Eréchnac *et al.* 1988; Pastor *et al.* 1988, 1989; Haberland *et al.* 1990; Kawai and Weare 1990; Rademann 1991; Kaiser and Rademann 1992; Zhao *et al.* 1994).

Among these divalent metal clusters Hg_n is the most intensively studied both experimentally and theoretically. Experiments on the ionisation potential

(Rademann *et al.* 1987; Haberland *et al.* 1990; Rademann 1991), inner-shell autoionisation spectra (Eréchnac *et al.* 1988) and photoelectron spectroscopy (Kaiser and Rademann 1992) of the Hg_n find a gradual transition from van der Waals-like to metallic properties in the size range between 20 and 70 atoms. Calculations on the size dependence of the ionisation energy and autoionisation energy of these clusters based on a tight-binding Hubbard Hamiltonian have shown that the transition from localised to delocalised electronic states occurs in Hg_n at $n \approx 13$ –19 (Pastor *et al.* 1988, 1989). In this paper, we shall use the localised orbital approach to calculate the ionisation potential of Hg_n clusters up to 55 atoms.

2. Theoretical Model

Due to the large number of electrons and the heavy nucleus in the Hg atom, an *ab initio* computation on the Hg_n cluster is almost impossible. A simplified theoretical method must be developed to investigate such a system. In this work we use a parametrised LCAO Hamiltonian constructed from the localised orbital theory (Weeks *et al.* 1973; Bullett and Cohen 1977; Heine 1980; Zhao *et al.* 1994). The atomic-like orbitals $|\phi_{il}\rangle$ are defined by the set of localised pseudopotential equations

$$(T + V_i)|\phi_{il}\rangle - \sum_{j'} (V_j^i - |\phi_{jl'}\rangle\langle\phi_{jl'}|V_j^i)|\phi_{il}\rangle = \epsilon_{il}|\phi_{il}\rangle. \quad (1)$$

Here i and l label the atomic site and angular momentum of the orbital respectively, V_i is the potential of the isolated atom i , V_j^i is the deviation of the crystal potential from V_i , caused by the presence of atom j , and T is the kinetic energy operator. We can write (1) in an alternative form:

$$H|\phi_{il}\rangle = \epsilon_{il}|\phi_{il}\rangle + \sum_{j'} |\phi_{jl'}\rangle\langle\phi_{jl'}|V_j^i|\phi_{il}\rangle = \sum_{j'} |\phi_{jl'}\rangle D_{jl',il} \quad (2)$$

by introducing the coefficient matrix D . By assuming linear independence of the localised orbitals, it has been proved that the eigenenergy E can be determined from the secular equation for the pseudo-Hamiltonian D matrix (Weeks *et al.* 1973),

$$|D - EI| = 0, \quad (3)$$

whose diagonal elements and off-diagonal elements are

$$D_{il,il} = \epsilon_{il} \approx \epsilon_{il}^0 - \sum_{j'} \langle\phi_{il}|\phi_{jl'}\rangle\langle\phi_{jl'}|V_j^i|\phi_{il}\rangle, \quad (4)$$

$$D_{il,jl'} = \langle\phi_{il}|V_j^i|\phi_{jl'}\rangle. \quad (5)$$

Here ϵ_{il}^0 is the atomic level (Pastor *et al.* 1988, 1989). In equation (4) we have neglected the crystal field integral because it is usually much smaller than the

hopping integral. In practice, the hopping integral in the D matrix is obtained from Slater's tight-binding formula. The Slater-Koster parameter is

$$V_{ll'm} = \eta_{ll'm} t. \quad (6)$$

Here we choose $\eta_{ss\sigma} = -1.32$, $\eta_{sp\sigma} = 1.42$, $\eta_{pp\sigma} = -2.22$, $\eta_{pp\pi} = -1.32$ and $t = 0.44$ eV (Pastor *et al.* 1988, 1989). For sp bonding, the distance dependence of the hopping integral is $t \sim d^{-2}$. The orbital overlap integral $\langle \phi_{il} | \phi_{jl'} \rangle$ is derived by employing the extended Hückel approximation ($K = 1.50$):

$$V_{ll'm} = S_{ll'm} \frac{K}{2} (\epsilon_l^0 + \epsilon_{l'}^0). \quad (7)$$

Thus, we can obtain the eigenenergy or the density of states by diagonalising the pseudo-Hamiltonian D matrix. Instead of a direct diagonalisation, we adopt the moment expansion method (Gaspard and Cyrot-Lackmann 1973; Heine 1980) to calculate the eigenenergy spectrum. The density of states (DOS) of the system is determined from the Green function (Heine 1980):

$$n(E) = -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0} G(E + i\epsilon). \quad (8)$$

The Green function is obtained via a continuous fraction whose coefficients are related to a certain amount of moment (Gaspard and Cyrot-Lackmann 1973). Comparing with direct diagonalisation, the moment method needs less computational time but can give quite accurate results.

After the total DOS has been obtained, the Fermi energy E_F of the cluster can be determined by requiring

$$\int_{-\infty}^{E_F} n(E) dE = \frac{1}{4}, \quad (9)$$

because the total number of electrons in full occupied s, p levels is eight while there are only two electrons in each Hg atom. Assuming that the shape of the DOS of Hg_n remains unchanged after ionisation, the size-dependent ionisation potential can be calculated from (Pastor *et al.* 1988, 1989; Zhao *et al.* 1994)

$$I_n = -E_F + \frac{1}{2} \frac{e^2}{R_n} = -E_F + \frac{1}{2} \frac{e^2}{r_0} n^{-1/3}. \quad (10)$$

Here the first term $-E_F$ denotes the energy needed to remove an electron from the highest occupied state of the cluster to the vacuum state. The second term arises from a classical static electric effect (Wood 1981; Perdew 1988), which can account for the shift of the electronic levels of Hg_n^+ with respect to those of neutral Hg_n upon ionisation. Here R_n is the cluster radius and r_0 the atomic radius. In most monovalent metal clusters such as Na_n or K_n , the electronic

structure of the cluster is considered to be similar to the bulk and consequently the $-E_F$ is replaced by the bulk work function W ; thus

$$I_n = W + \frac{1}{2} \frac{e^2}{R} = W + \frac{1}{2} \frac{e^2}{r_0} n^{-1/3}. \quad (11)$$

This simple model, usually called the conducting sphere droplet (CSD) model (Wood 1981; Perdew 1988), has been applied to the simple metal clusters quite successfully, but fails in predicting the size-dependent ionisation potential of the transition metal cluster (Zhao *et al.* 1993) due to the localised d band.

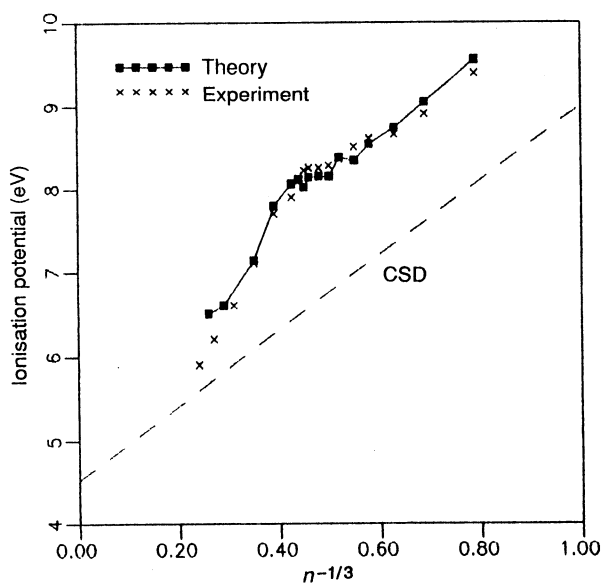


Fig. 1. Size dependence of the ionisation potential I_n of Hg_n clusters. The calculated results of the localised orbital theory are shown along with the experimental results taken from (Rademann *et al.* 1987; Rademann 1991). The dashed line is the theoretical prediction of the conducting sphere droplet (CSD) model.

3. Results and Discussion

In small clusters ($n < 13$) the cohesion is mainly van der Waals-like. Therefore, these clusters favour a close-packing structure with a compactness or mean coordination number as high as possible. Here we adopt those polyhedral structures with the highest compactness which are similar to those that have been obtained for small Mg_n clusters (Kumar and Car 1991). For larger clusters, we adopt the fcc-like packing structures, e.g. cuboctahedron or truncated tetrahedron, since the lattice structure of bulk Hg can be viewed as a slightly distorted fcc structure. The calculated ionisation potential and the experimental values (Kawai

and Weare 1990) are shown in Fig. 1. The present results based on the localised orbital theory conform nicely to the experiments.

In Fig. 1 there is an obvious transition behaviour at about $n = 13$ in the size dependence of the ionisation potential both theoretically and experimentally. Below the transition point ($n < 13$), I_n evolves gradually with increasing cluster size. Beyond that ($n > 13$) I_n decreases dramatically with n . This rapid change is believed to correspond to the transition from the localised electronic state (van der Waals) to the more delocalised one (covalent or metallic). In Fig. 1 we observe that there is not much discrepancy between I_n and the prediction of the CSD model up to $n = 70$, indicating that clusters of this size are almost metallic.

Previously, Pastor *et al.* (1988, 1989) performed a tight-binding calculation on the ionisation potential of Hg_n clusters but obtained relatively poor agreement with experiment in the medium size range. They explained the failure by strong electron localisation originating from electronic correlation. However, we believe this is not the only reason. As the cluster is very small, the electronic correlation and localisation in the cluster can be much stronger than that in the larger one. Then the deviation of the theory from experiment much be larger in the smallest clusters and decrease as the cluster becomes larger. In contrast to this view, the disagreement between their calculation and the experimental results lies just in the medium size range ($5 < n < 50$). Therefore, electronic correlation is not the only reason. Since the overlap between different atomic orbitals is neglected in their model, we believe that the improvement in our theory comes from the inclusion of the overlap effect in the diagonal terms of the pseudo-Hamiltonian matrix D . In the tight-binding localised orbital theory, correction of the overlap effect can provide the repulsive interaction between each atom and weaken the attractive cohesion. As a result, localisation of electrons in the clusters is more pronounced than in the usual tight-binding theory. However, as the cluster becomes larger and almost metallic, the localised orbital theory can overestimate the electronic localisation and cannot serve as well as it does in small clusters. From Fig. 1 we find that the disagreement between theory and experiment becomes non-negligible when the cluster size exceeds 50.

In summary, the localised orbital theory can describe the electronic structure and size dependent ionisation potentials of Hg_n clusters smaller than 50 atoms, while the tight-binding model (Pastor *et al.* 1988, 1989) should be used in the larger clusters.

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