Unrestricted Hartree-Fock Calculation of the Ionization Potential of Small Hg_n Clusters.

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Abstract. – The ionization potential of small Hg_n clusters has been calculated. For the first time good agreement with experimental results has been obtained. It is shown that interatomic Coulomb interactions are important. The energy of Hg_n^+ is calculated using the unrestricted inhomogeneous Hartree-Fock approximation. As a consequence of a change in the charge distribution in Hg_n^+, we obtain an abrupt change in the slope of the ionization potential at the critical cluster size $n_{cr} \sim 14$. The presented results are expected to be valid for covalent clusters in between ionized van der Waals clusters and metallic clusters.

The size dependence of the electronic properties of small clusters is an important problem in cluster physics. Particularly interesting is the transition from van der Waals (VDW) to covalent to metallic bonding in neutral Hg_n clusters for increasing cluster size [1-5].

The nature of the chemical bonding in Hg_n^+ clusters remains unclear. The positive charge may be either localized within a subcluster Hg_i^+ ($i \leqslant n$), as in ionized VDW systems [3,6,7], or delocalized, as in ionized metallic clusters.

Therefore, it is important to study the ionization potential (*IP*), since it reflects the combined properties of the neutral and ionized clusters. Experiments [1,3] show an abrupt change in the slope of the *IP* of Hg_n clusters for $n_c \sim 13$. It is the purpose of this letter to calculate the *IP*(n) of Hg_n clusters, taking into account explicitly the properties of the ionized clusters.

A two-band Hubbard Hamiltonian including interatomic Coulomb repulsion, charge-dipole and dipole-depole interactions between nearest neighbours (n.n.) is used:

$$H = H_1 + H_h, \qquad H_1 = H_0 + H_{cd} + H_{dd}, \tag{1}$$

with

$$H_0 = \sum_{i\sigma} \varepsilon_s n_{is\sigma} + \sum_{i\gamma\sigma} \varepsilon_\gamma n_{i\gamma\sigma} + \sum_i U_{ss} n_{is\uparrow} n_{is\downarrow} +$$
$$+ \sum_{i,\,\gamma\sigma \neq \beta\sigma'} U_{pp} n_{i\gamma\sigma} n_{i\beta\sigma'} + \sum_{i\gamma\sigma\sigma'} U_{sp} n_{is\sigma} n_{i\gamma\sigma'} + \frac{1}{2} \sum_{\langle i,j \rangle} G q_i q_j. \tag{2}$$

Here, ε_s, ε_γ refer to the s and p atomic energy levels ($\gamma = p_x, p_y, p_z$). U_{ss}, U_{pp} and U_{sp} are the

intra-atomic Coulomb interaction energies. The last term in eq. (2) describes n.n. interatomic Coulomb interactions G, assumed to be the same for electron-electron, electron-core and core-core interactions. $q_i = e\left(2 - \sum_\sigma n_{is\sigma} - \sum_{\gamma\sigma} n_{i\gamma\sigma}\right)$ is the charge operator at the site i (with $n_{i\gamma\sigma} \equiv c_{i\gamma\sigma}^\dagger c_{i\gamma\sigma}$). $c_{i\gamma\sigma}^\dagger$, $c_{i\gamma\sigma}$ are the usual creation and annihilation operators. The charge-dipole H_{cd} and dipole-dipole H_{dd} terms have the usual form [1], and the kinetic energy is given by

$$H_h = \sum_{\langle ij\rangle\sigma} t_{ss} c_{is\sigma}^\dagger c_{js\sigma} + \sum_{\langle ij\rangle\gamma\beta\sigma} t_{pp}^{i\gamma,j\beta} c_{i\gamma\sigma}^\dagger c_{j\beta\sigma} + \sum_{\langle ij\rangle\gamma\sigma} t_{sp}^{i,j\gamma} c_{is\sigma}^\dagger c_{j\gamma\sigma}. \tag{3}$$

Here, t_{ss}, $t_{pp}^{i\gamma,j\beta}$ and $t_{sp}^{i,j\beta}$ (γ, $\beta = p_x$, p_y, p_z) refer to the hopping integrals between nearest neighbours. Then, the IP can be calculated from

$$IP(n) = E(\mathrm{Hg}_n^+) - E(\mathrm{Hg}_n) + \frac{3}{8}\left(\frac{e^2}{R_n}\right), \tag{4}$$

where R_n is the radius of the cluster. The last term arises from long-range Coulomb interactions which are not included in the ground-state energies $E(\mathrm{Hg}_n^+)$ and $E(\mathrm{Hg}_n)$ resulting from the Hamiltonian of eq. (1) [8].

The energies E are now calculated as follows. It is straightforward to rewrite H_1 as

$$H_1 = -\frac{3}{4} z_b \Delta \left(\frac{\alpha}{d^3}\right)^2 - 2 \sum_i z_i \bar{E}_p + H_0(\tilde{\varepsilon}_s^i, \tilde{\varepsilon}_\gamma^i, \tilde{U}_{sp}^i, \tilde{G}_{ij}), \tag{5}$$

by eliminating H_{cd} and H_{dd} using second-order perturbation theory. The first term is London's dispersion formula and results from H_{dd} [9]. z_b is the number of bonds in the cluster, d the interatomic distance, α refers to the s-p electronic contribution to the atomic polarizability, and $\Delta = \varepsilon_\gamma - \varepsilon_s$. The second term results from H_{cd}. z_i is the coordination number of atom i and $\bar{E}_p = E_p - (3/8)\Delta(\alpha/d^3)^2$, with $E_p = 1/2(\alpha e^2/d^4)$. The last term describes the renormalization of the parameters of eq. (2) due to H_{cd} and H_{dd} [2]. The site-dependent renormalized quantities are $\tilde{\varepsilon}_s^i = \varepsilon_s + z_i \bar{E}_p$, $\tilde{\varepsilon}_\gamma^i = \varepsilon_\gamma + 3z_i \bar{E}_p$, and $\tilde{U}_{sp}^i = U_{sp} + 2z_i \bar{E}_p$ [3]. The renormalized interatomic interactions are given approximately for f.c.c. like clusters by $\tilde{G}_{ij} = G - \bar{E}_p[z_{lm} + 0.6034(z_l + z_m - 2z_{lm})$ (see [3]), where z_{lm} is the number of neighbours shared by l and m plus 1. Note that the total Hamiltonian (eq. (1)) has been transformed into an effective two-band Hubbard Hamiltonian $H = H_1 + H_h$. For this we calculate the ground state of Hg_n and Hg_n^+ in the unrestricted Hartree-Fock approximation. We use $n_{i\mu\sigma} n_{i\nu\sigma'} = n_{i\mu\sigma}\langle n_{i\nu\sigma'}\rangle + n_{i\nu\sigma'}\langle n_{i\mu\sigma}\rangle - \langle n_{i\mu\sigma}\rangle\langle n_{i\nu\sigma'}\rangle$, where μ, $\nu = s$, p_x, p_y, p_z, which

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[1] $H_{cd} = \sum_{ij} eq_i \dfrac{\boldsymbol{R}_{ji}\cdot\boldsymbol{p}_j}{|\boldsymbol{R}_{ji}|^3}$, $H_{dd} = \dfrac{1}{2}\sum_{ij}\left(\dfrac{\boldsymbol{p}_i\cdot\boldsymbol{p}_j}{|\boldsymbol{R}_{ji}|^3} - 3\dfrac{\boldsymbol{p}_i\cdot\boldsymbol{R}_{ji}\boldsymbol{p}_j\cdot\boldsymbol{R}_{ji}}{|\boldsymbol{R}_{ji}|^5}\right)$, where $\boldsymbol{p}_i$ denotes the dipole operator at site i and $\boldsymbol{R}_{ji} = \boldsymbol{R}_j - \boldsymbol{R}_i$.

[2] While H_{cd} does not modify the ground state of $\mathrm{Hg}_n(|\Psi_0\rangle)$, it changes, together with H_{dd}, the energy by $- z_i|q_i|[E_p - (3/8)\Delta(\alpha/d^3)^2]$ for a state with charge q_i on atom i. z_i is the coordination number of atom i. The contribution $(3/8)\Delta(\alpha/d^3)^2$ describes the weakening of the van der Waals interactions due to the absence of an electron.

[3] H_{cd} and H_{dd} affect, in second-order perturbation energy, the energy of the ground state of H_0 and the energy of the local excitations $6s^1 6p^0$, $6s^2 6p^1$, and empty of atom i (while all other atoms are in the $6s^2 6p^0$ state). This is represented by the renormalizations $\tilde{\varepsilon}_s^i = \varepsilon_s + z_i\bar{E}_p$, $\tilde{\varepsilon}_\gamma^i = \varepsilon_\gamma + 3z_i\bar{E}_p$, and $\tilde{U}_{sp}^i = U_{sp} 2z_i\bar{E}_p$. The corresponding renormalized interatomic Coulomb interaction ($\tilde{G}_{ij}$) is obtained by calculating the correction resulting from $\bar{H}_{cd}$ to the excited state $|\Psi_{lm\sigma}\rangle = c_{l\gamma\sigma}^\dagger \chi_{\mu s\sigma}|\Psi_0\rangle$. How these

causes a shift of the energy levels. The operators describing the interatomic Coulomb interactions are approximated by $c_{i\mu\sigma}^\dagger c_{i\mu\sigma} c_{j\nu\sigma'}^\dagger c_{j\nu\sigma'} = \langle c_{i\mu\sigma}^\dagger c_{i\mu\sigma} \rangle c_{j\nu\sigma'}^\dagger c_{j\nu\sigma'} + c_{j\mu\sigma}^\dagger c_{j\mu\sigma} \langle c_{j\nu\sigma'}^\dagger c_{j\nu\sigma'} \rangle - \langle c_{i\mu\sigma}^\dagger c_{i\mu\sigma} \rangle \langle c_{j\nu\sigma'}^\dagger c_{j\nu\sigma'} \rangle + \dots$. The resulting effective mean-field Hamiltonian is then

$$H = \sum_{i\sigma} E_{is\sigma} c_{is\sigma}^\dagger c_{is\sigma} + \sum_{i\gamma\sigma} E_{i\gamma\sigma} c_{i\gamma\sigma}^\dagger c_{i\gamma\sigma} + \sum_{\langle ij\rangle \sigma} T_{ss\sigma}^{ij} c_{is\sigma}^\dagger c_{js\sigma} + \sum_{\langle ij\rangle \gamma\sigma} T_{sp\sigma}^{i,j\gamma} c_{is\sigma}^\dagger c_{j\gamma\sigma} + $$

$$+ \sum_{\langle ij\rangle \sigma\beta} T_{pp\sigma}^{i\beta,j\gamma} c_{i\beta\sigma}^\dagger c_{j\gamma\sigma} + H_C, \qquad (6)$$

with the renormalized energies (see [1])

$$E_{is\sigma} = \tilde{\varepsilon}_s^i + U_{ss} \langle n_{is\sigma} \rangle + \sum_{\gamma\sigma'} \tilde{U}_{sp}^i \langle n_{i\gamma\sigma'} \rangle - 2 \sum_{j\neq i} \tilde{G}_{ij} + \sum_{j\neq i\sigma'} \tilde{G}_{ij} \langle n_{js\sigma'} \rangle + \sum_{j\neq i,\,\gamma\sigma'} \tilde{G}_{ij} \langle n_{j\gamma\sigma'} \rangle,$$

$$E_{i\gamma\sigma} = \tilde{\varepsilon}_\gamma^i + \sum_{\beta\sigma'\neq \gamma\sigma} U_{pp} \langle n_{i\beta\sigma'} \rangle + \sum_{\sigma'} \tilde{U}_{sp}^i \langle n_{is\sigma'} \rangle - 2 \sum_{j\neq i} \tilde{G}_{ij} + \sum_{j\neq i,\,\beta\sigma'} \tilde{G}_{ij} \langle n_{j\beta\sigma'} \rangle + \sum_{j\neq i\sigma'} \tilde{G}_{ij} \langle n_{js\sigma'} \rangle,$$

and the renormalized hopping integrals

$$T_{ss\sigma}^{ij} = t_{ss} - \tilde{G}_{ij} \langle c_{js\sigma}^\dagger c_{is\sigma} \rangle, \qquad T_{sp\sigma}^{i,j\gamma} = t_{sp}^{i,j\gamma} - \tilde{G}_{ij} \langle c_{j\gamma\sigma}^\dagger c_{is\sigma} \rangle, \qquad T_{pp\sigma}^{i\beta,j\gamma} = t_{pp}^{i\beta,j\gamma} - \tilde{G}_{ij} \langle c_{j\beta\sigma}^\dagger c_{i\gamma\sigma} \rangle.$$

In eq. (6), H_C is a scalar which includes the VDW energy in second-order perturbation theory [9] and which takes care of the double-counting terms of the Hartree-Fock approximation. Two occupation numbers per site and six mean values per each bond have been calculated self-consistently in order to obtain the ground-state energies $E(\text{Hg}_n^+)$ and $E(\text{Hg}_n)$.

$E(\text{Hg}_n^+)$ and $E(\text{Hg}_n)$ are calculated as a function of the cluster size for $2 \leqslant n \leqslant 55$, using for the atomic s-p average energy gap $\Delta = 5.8$ eV and $U = U_{ss} = U_{sp} = U_{pp} = 7.5$ eV. The other parameters, G and $t_{\gamma\beta}$, are allowed to vary. Note that a reasonable value for the interatomic Coulomb interaction G should be around 4 eV, which is approximately the bare interaction between two unit charges separated by the interatomic distance ($d = 3.36$ Å). The values of t_{sp} and t_{ss} were assumed to be proportional to t_{pp} [10] [4]. For simplicity, we replace the p_x, p_y and p_z orbitals by one s-like p-state at each site. This does not affect the ground-state energy at least in lowest order of H_h. From the atomic polarizability we get the value $E_p = 0.29$ eV as an upper bound for E_p. $\tilde{E}_p$ has a smaller value due to the renormalization produced by the effect of H_{dd} (see [2]). In order to compare with the experimental results we shift the calculated values for IP by a constant, which is determined by fitting to the experimental IP of the dimer.

Results obtained for IP are shown in fig. 1 and 2. In fig. 1 we compare our results obtained from diagonalization of H (eq. (6)) and using eq. (4) for the IP, with the experiments performed by Rademann *et al.* [1] and Haberland *et al.* [3]. Note that good agreement with the experiment by Rademann *et al.* is obtained, at least qualitatively. $t_{pp} = 0.$ 4 eV yields best

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renormalizations come about in detail can be understood by noting that, for instance, for the excitation $|\Psi_{lm\sigma}\rangle$ one calculates straightforwardly the energy correction $\Delta E_{lm\sigma} = -z_l \tilde{E}_p - z_m \tilde{E}_p +$

$+ \tilde{E}_p \left\{ 1 + 2d^4 \sum_{i\neq m\neq l} \boldsymbol{R}_{li} \cdot \boldsymbol{R}_{mi} / (|\boldsymbol{R}_{li}|^3 |\boldsymbol{R}_{li}|^3) \right\}$. The first two terms contribute to the renormalization of

U_{sp}, while the last one contributes to $(-G)$. In an f.c.c. structure there are four types of n.n. Those neighbours common to both atom l and atom m give a contribution E_p. The others contribute E_p reduced by factors $1/\sqrt{2}$, $1/\sqrt{3}$ and $1/2$, respectively. Hence, the average contribution is 0.6034.

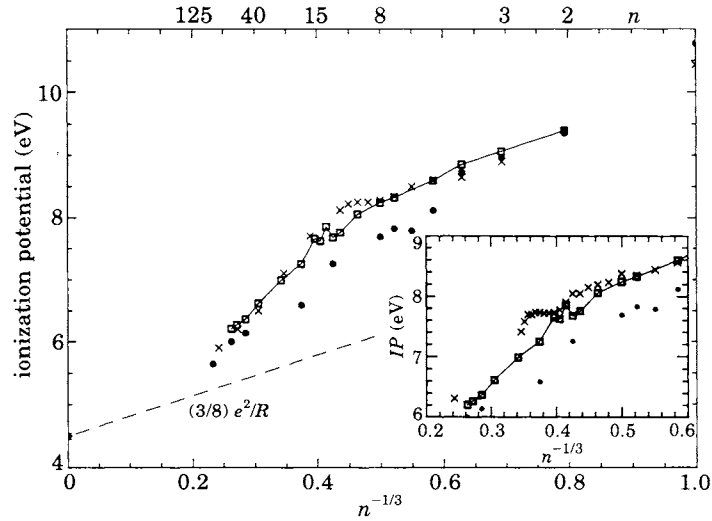[4] We use for the hopping elements the relation $t_{ss} = t_{pp} = -0.6t_{pp}$.

Fig. 1. – Results for the size dependence of the ionization potential IP of Hg_n calculated from $IP(n) =$ $= E(Hg_n^+) - E(Hg_n) + 3e^2/8R$ ($\square$) compared with previous tight-binding (TB) calculations (ref. [5]) ($\bullet$) and with photoionization experiment (ref. [1]) ($\times$). The inset figure shows electron impact ionization experimental results (ref. [3]) ($\times$). Note that $3e^2/8R_n$ is expected for metallic spheres. In the present work $U = 4\,eV$, $G = 3\,eV$, $\Delta = 4\,eV$, $t_{pp} = 0.4\,eV$, $\tilde{E}_p = 0$.
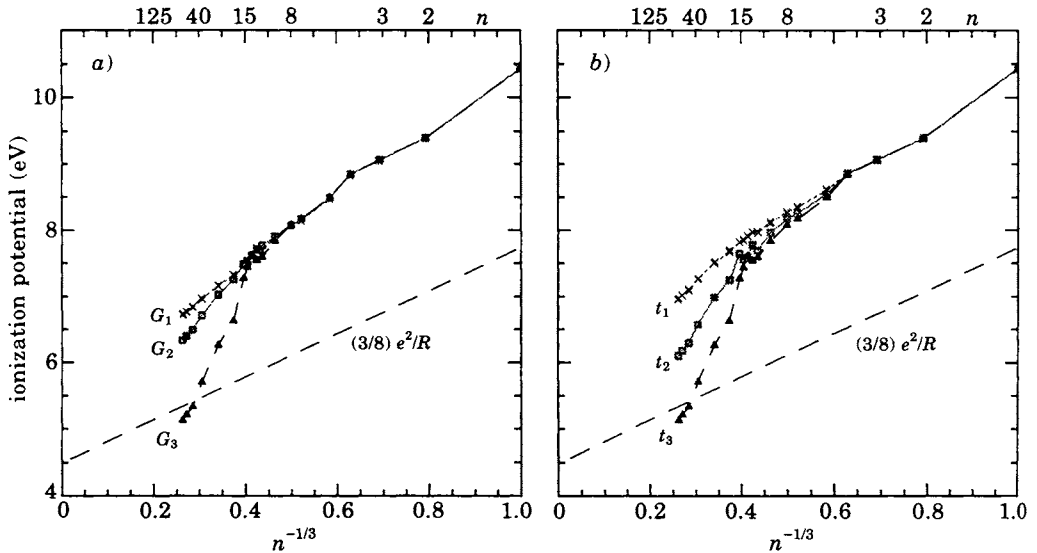

Fig. 2. – Dependence of the ionization potential $IP(n)$ on the interatomic Coulomb repulsion G and the hopping elements ($t_{pp} = t$). For the very small clusters our model is not valid. a) $G_1 = 3\,eV$, $G_2 = 4\,eV$, $G_3 = 5\,eV$, $t_{pp} = 0.7\,eV$, $U = 7.5\,eV$, $\Delta = 5.8\,eV$; b) $t_1 = 0.3\,eV$, $t_2 = 0.4\,eV$, $t_3 = 0.5\,eV$, $G = 5\,eV$.

agreement with experiment. From bulk properties one would estimate an effective $T_{pp} =$ $= 1\,eV$ [5]. The values used for Δ, U and G are consistent with optical data [11]. For simplicity, we assume $\tilde{E}_p = 0$, *i.e.* we neglect the influence of charge-dipole interactions. The

calculations yield definitely a change in the slope of *IP* vs. cluster size. The explicit calculation of the energy of the ionized clusters taking into account interatomic Coulomb interactions is essential for this. The subfigure refers to experimental results by Haberland *et al.* [3] obtained from electron impact ionization. The results of the main figure were obtained by assuming compact symmetric cluster structures [5] (which maximize the number of bonds) and no relaxation of the structures has been taken into account. In fig. 2a) and b) we present results for the *IP* as a function of the cluster size for different values of G and t_{pp}, respectively, in order to illustrate the dependence of our results on these parameters. Note that as G increases from 3 eV to 4 eV, a small change in the slope of the *IP* occurs at $n \simeq 19$. For $G = 5$ eV, a remarkable change in the slope of *IP* can be observed at $n = 15$. Then, at $n = 19$ and at $n = 43$ a decrease in the slope of *IP* occurs.

To check on the decoupling approximation used for $n_{i\mu\sigma}$, $n_{j\nu\sigma'}$ we compare our results for $E(\mathrm{Hg}_n)$ and $E(\mathrm{Hg}_n^+)$ with those obtained by using exact diagonalization for $n = 2$. The results for the energy coincide in order t_{sp}^2/Δ for the neutral and in order t_{sp} for the ionized dimer (note that $t_{sp}^2 \ll \Delta$). For the latter there are small differences of order t_{sp}^2/Δ which do not alter the trends as the parameters are varied. This agreement justifies the decoupling approximation also for larger clusters.

In order to better understand the physical origin of the change in the slope of the *IP*, we have examined the charge distribution in Hg_n^+. We obtain an abrupt change in the charge distribution from $n = 14$ to $n = 15$. For $n \leq 14$ the positive charge is distributed mainly at the surface of the cluster, while 76% of the charge is at the central atom for $n = 15$. Already 83% of the positive charge concentrates at the centre of the cluster for $n = 16$, 94% for $n = 19$ and 99% for $n = 55$. In fact the charge distribution of larger clusters ($13 < n < 55$) oscillates. The positive charge is at the centre and at the surface, while, in between, the first atomic coordination shell is negatively charged. This can be understood in terms of perturbation theory. For Hg_n^+ and $\bar{E}_p = 0$ the ground-state energy of $H = H_1 + H_\mathrm{h}$ is in second order in H_h approximately given by $E_n(\mathrm{Hg}_n^+) \simeq -b_n t_{ss} - O(t_{sp}^2/(\Delta + U - G)) - O(t_{sp}^2/(\Delta + U - 2G)) + \dots$. As regards delocatization the most important term is the one proportional to t_{ss}, where b_n is a constant of the order of 1 ($b_n = 1$ for $n = 1, 2, 3, 4$, $b_5 = 1.64$). The last two contributions regulate the charge distribution within the cluster and arise from hopping processes involving intra- and intershell transitions, where the shells are defined with respect to the charged atom. In particular, the last term arises from hopping of an electron from the second to the first shell. Note that via G the charge configuration involving two positively charged sites separated by a negative-charge site in between lowers the energy. Such excited states with a charge distribution lowering the cluster energy can only exist for $n \geq 14$. In those clusters electrons may be transferred from the second coordination shell, which then becomes positively charged, to the first shell that surrounds the positively charged central atom. Consequently, the dependence of $[E(\mathrm{Hg}_n^+) - E(\mathrm{Hg}_n)]$ on n changes for $n \geq 14$. Then, a decrease in the slope of *IP* occurs when the second coordination shell is complete at $n = 43$. The clusters having 19, 43 and 55 atoms have closed shell and point group O_h symmetry. For these, further added atoms have lower number of n.n. in the first coordination shell and therefore the number of *new* hopping processes which lower the interatomic repulsion energy of Hg_n^+ decreases. This is expected to be particularly noticeable for $n = 55$, since this is the largest cluster in which all atoms have n.n. belonging to the first coordination shell. $n_\mathrm{c} = 14$ is the critical size, since only for $n = 14$ one obtains nearly the same energy if the positive charge is mainly at the centre or at the surface of the cluster.

The intershell hopping for clusters with $n \geq 14$ can be interpreted as follows: in the ionized clusters the positive charge is situated at the centre and induces a radial polarization of the covalent bonds between remaining neutral atoms, in order to lower the Coulomb energy. This induced polarization of the covalent bonds represents the main screening process of a

weak covalent system. In the VDW region $(n < n_c)$, screening arises from atomic polarization [4], which we do not take into account, since we neglected charge-dipole interactions. Note that for small van der Waals clusters, the term $(3/8)\,e^2/R$ in eq. (4), used for the calculation of $IP(n)$, is no longer valid. Therefore, we do not expect our model to describe properly the small ionized VDW clusters. Particularly, the IP discrepancy present for $8 \leqslant n \leqslant 13$ may result from not properly taking care of the influence of the VDW interactions in Hg_n on the renormalization of the hopping elements. For large clusters with $n \geqslant 80$ our calculations, which become too time consuming, should take into account the influence of metallic screening on the model parameters, in order to give a realistic description of the IP.

In summary, our calculations show that the behaviour of the IP is, for a certain range of cluster sizes, dominated by the properties of the ionized clusters, and that the size dependence of IP, particularly in the covalent region $(13 < n \lesssim 80)$, can be well described by a picture of a localized positive charge surrounded by polarized covalent bonds.

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