

# Theory for the optical properties of small $\text{Hg}_n$ clusters

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**Abstract.** The static and dynamical polarizabilities of the Hg-dimer are calculated by using a Hubbard Hamiltonian to describe the electronic structure. The Hamiltonian is diagonalized exactly within a subspace of second-quantized electronic states from which only multiply ionized atomic configurations have been excluded. With this approximation we can describe the most important electronic transitions including the effect of charge fluctuations. We analyze the polarizability as a function of the intraatomic Coulomb interaction which represents the repulsion between electrons. We obtain that this interaction results in strong electronic correlations in the excited states and increases the first excitation energy of the dimer by 0.8 eV in comparison to a calculation which neglects correlations, resulting in a better agreement with the experiment.

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## 1. Introduction

We have calculated the dynamical polarizability  $\alpha(\omega)$  and the electronic structure of the Hg-dimer as a first step to discuss the size dependence of the optical properties of  $\text{Hg}_n$ -clusters. We discuss the competition between electron delocalization (due to hopping) and electronic correlations (due to the Coulomb interaction between electrons).

Experimentally, the optical spectrum of  $\text{Hg}_2$  consists of two absorption lines [1] at 4.9 eV and at 6.1 eV. The line at 6.1 eV is rather intense and corresponds to a transition from the singlet ground state of  $\text{Hg}_2$  to a singlet excited state. The other line corresponds to a transition to a triplet excited state and is of low intensity, because this

transition arises only due to spin-orbit coupling. It is important to note, that these two absorption lines of  $\text{Hg}_2$  are close to the corresponding absorption lines of single Hg atoms. Previous calculations [2, 3] would have yielded an absorption line for  $\text{Hg}_2$  which is about 1 eV below the corresponding atomic line and which is thus in strong disagreement with experiment. It is the purpose of this paper to improve previous calculations by using a better treatment of the electron-electron interactions. As a first step we neglect for simplicity spin-orbit interactions and thus the singlet-triplet optical excitation. This permits also a closer comparison with previous calculations. Within our theory it is of course also possible to determine the singlet-triplet optical excitation. Since the exchange interaction between valence electrons in atoms is of the order of 1 eV, we expect that the singlet-triplet absorption line is about 1 eV below the singlet-singlet line and of decreased intensity, according to the strength of the spin-orbit interaction.

## 2. Model

The electronic structure of the Hg-dimer is obtained by using a Hubbard Hamiltonian for the valence electrons

$$\begin{aligned}
 H = & \sum_{i,\alpha,\sigma} \varepsilon_\alpha \hat{n}_{i\alpha\sigma} + \sum_{i,j,\alpha,\beta,\sigma} t_{ij\alpha\beta} c_{i\alpha\sigma}^\dagger c_{j\beta\sigma} \\
 & + U \sum_{\substack{i,\alpha,\beta,\sigma,\sigma' \\ (\alpha,\sigma) \neq (\beta,\sigma')}} \hat{n}_{i\alpha\sigma} \hat{n}_{i\beta\sigma'}, \quad (1)
 \end{aligned}$$

where  $i$  and  $j$  refer to atom position,  $\alpha$  and  $\beta$  to orbital ( $s, p_x, p_y, p_z$ ) and  $\sigma, \sigma'$  to spin,  $c_{i\alpha\sigma}^\dagger$  and  $c_{j\beta\sigma}$  are the creation and annihilation operators,  $\hat{n}_{i\alpha\sigma} = c_{i\alpha\sigma}^\dagger c_{i\alpha\sigma}$  the electron number operators,  $\varepsilon_\alpha$  are the atomic levels,  $t_{ij\alpha\beta}$  the hopping parameters and  $U$  the effective Coulomb interaction.  $U$  is defined as the difference between the Coulomb interaction  $U_0$  between two electrons in the same atom and the Coulomb interaction between one electron in atom 1 (coordinates:  $-d/2, 0, 0$ ) and the other electron in atom 2 (coordinates:  $d/2, 0, 0$ ), thus  $U = U_0 - e^2/d$ , where  $d$  is the

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interatomic distance. All parameters are taken from [2]. The diagonalization of this Hamiltonian yields the ground state, excited states and their energies.

The ground state  $\Phi_0$  of energy  $E_0$  is symmetric with respect to the exchange of atoms. It consists mainly of the neutral configuration, where all 4 electrons are in  $s$ -levels, thus  $\Phi_0 \simeq c_{1s\uparrow}^+ c_{1s\downarrow}^+ c_{2s\uparrow}^+ c_{2s\downarrow}^+ |0\rangle$ .

The excited states  $\Phi_n$ , which can be reached by dipole transitions, can be classified in two categories according to the orientation of the external electric field with respect to the bond. First, when the electric field is parallel to the bond, the excited states are antisymmetric with respect to the exchange of atoms. There are two important configurations, a neutral excited configuration ( $\text{Hg}^*\text{Hg}$ ) formed by an antisymmetric linear combination of  $(c_{1s\uparrow}^+ c_{1p_x\downarrow}^+ c_{2s\uparrow}^+ c_{2s\downarrow}^+ |0\rangle + \text{permutations})$  and an ionic configuration ( $\text{Hg}^+\text{Hg}^-$ ) formed by an antisymmetric linear combination of  $(c_{1s\uparrow}^+ c_{2p_x\downarrow}^+ c_{2s\uparrow}^+ c_{2s\downarrow}^+ |0\rangle + \text{permutations})$ . This results in two excited states  $\Phi_n \simeq a_n(\text{ionic config.}) + b_n(\text{neutral config.})$  ( $n = 1, 2$ ) of low energy  $E_n$ . Note that the probability of an ionic configuration in these excited states is then given by  $P(\text{ionic config.}) \simeq |a_n|^2$ . Second, when the electric field is perpendicular to the bond, the excited states are antisymmetric with respect to a rotation of  $180^\circ$  around the bond axis. Similarly to the first case, a neutral excited configuration  $(c_{1s\uparrow}^+ c_{1p_y\downarrow}^+ c_{2s\uparrow}^+ c_{2s\downarrow}^+ |0\rangle + \text{permutations})$  and an ionic configuration  $(c_{1s\uparrow}^+ c_{2p_y\downarrow}^+ c_{2s\uparrow}^+ c_{2s\downarrow}^+ |0\rangle + \text{permutations})$  are important. As before, two excited states  $\Phi'_n$  of low energy  $E'_n$  ( $n = 1, 2$ ) are obtained.

The energies  $E_0$ ,  $E_n$  and  $E'_n$  and states  $\Phi_0$ ,  $\Phi_n$  and  $\Phi'_n$  obtained from the diagonalization of the Hamiltonian are now used to determine the dynamical polarizability  $\alpha_{il}(\omega)$ :

$$\alpha_{il}(\omega) = \frac{e^2}{\hbar} \sum_n |\langle n | \hat{p}_l | \Phi_0 \rangle|^2 \left( \frac{1}{\omega_{n0} + \omega + i\Gamma/2} + \frac{1}{\omega_{n0} - \omega - i\Gamma/2} \right), \quad (2)$$

where the sum is done over excited states  $|n\rangle$  and  $\omega_{n0}$  is the energy of the transition. Here  $l$  refers to the  $x$ -axis ( $|n\rangle = \Phi_n$ ) or to the  $y$  or  $z$ -axis ( $|n\rangle = \Phi'_n$ ). The damping factor in our calculation is  $\Gamma = 0.01$  a.u. The dipole matrix elements are obtained from a second quantized representation of the dipole moment operator:

$$\hat{p}_x = \frac{d}{2} \left( \sum_{\alpha, \sigma} \hat{n}_{2\alpha\sigma} - \sum_{\alpha, \sigma} \hat{n}_{1\alpha\sigma} \right) + \chi_{11} \sum_{\sigma, i} (-1)^{i-1} (c_{i p_x \sigma}^+ c_{i s \sigma} + c_{i s \sigma}^+ c_{i p_x \sigma}) \quad (3)$$

and

$$\hat{p}_y = \chi_{11} \sum_{\sigma, i} (c_{i p_y \sigma}^+ c_{i s \sigma} + c_{i s \sigma}^+ c_{i p_y \sigma}), \quad (4)$$

where  $\chi_{11}$  is obtained from the atomic polarizability. Note that  $\hat{p}_z$  is essentially the same as  $\hat{p}_y$  and that  $\alpha_{zz} = \alpha_{yy}$ , thus the average polarizability is

$$\alpha_{av} = (\alpha_{xx} + 2\alpha_{yy})/3. \quad (5)$$

Finally, the absorption cross section is

$$\sigma(\omega) \propto \omega \text{Im} \alpha_{av}(\omega). \quad (6)$$

### 3. Results

The experimental value of the Hg-dimer bond length is  $d = 3.3$  Å [4]. The hopping parameters are:  $t_{ss} = -0.017$  a.u.,  $t_{sp} = -0.018$  a.u.,  $t_{pp\sigma} = -0.028$  a.u. and  $t_{pp\pi} = -0.008$  a.u. [2]. The average value of the atomic  $sp$  excitation energy is  $\Delta = \varepsilon_p - \varepsilon_s = 0.213$  a.u. [2]. The bare intraatomic  $U_0 = 0.306$  a.u., from [2], results in an effective  $U = 0.147$  a.u. for the dimer. Finally,  $\chi_{11} = 1.354$  a.u. is obtained from the experimental static polarizability.

The comparison in Fig. 1 of  $\text{Im}[\alpha_{av}]$  for  $U = 0$  (upper panel neglecting charge fluctuations) and  $U = 0.147$  a.u. (lower panel, including correctly charge fluctuations) indicates the importance of electron correlations in the optical properties of the Hg-dimer. Three strong absorption peaks appear for  $U = 0$ . The two peaks which are lower in energy, nearly collapse in one for  $U = 0.147$  and the other peak practically vanishes in intensity.

The peak which is lowest in energy, comes from the absorption of the dimer for an electric field parallel to the bond and corresponds to the transition  $\Phi_0 \rightarrow \Phi_1$ . This peak increases in energy by  $0.029$  a.u. when  $U$  increases from 0 to  $0.147$  a.u. This behaviour is explained by increasing correlations. For  $U = 0$  there are no correlations and the weights of the ionic and neutral configurations are nearly the same (see Fig. 2). For  $U = 0.147$  a.u. this excit-

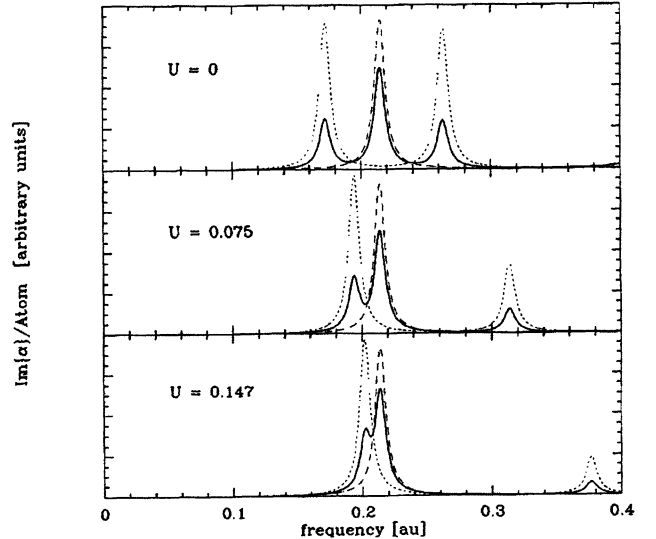


Fig. 1. Imaginary part of the dynamical polarizability (related to optical absorption) for different values of the effective Coulomb interaction  $U$ . Solid line: average polarizability  $\alpha_{av}$ . Long-dashed line: polarizability for an electric field oriented perpendicularly to the bond  $\alpha_{yy}$ . Short-dashed line: polarizability for an electric field oriented parallel to the bond  $\alpha_{xx}$ . Note that the lower panel actually corresponds to  $\text{Hg}_2$

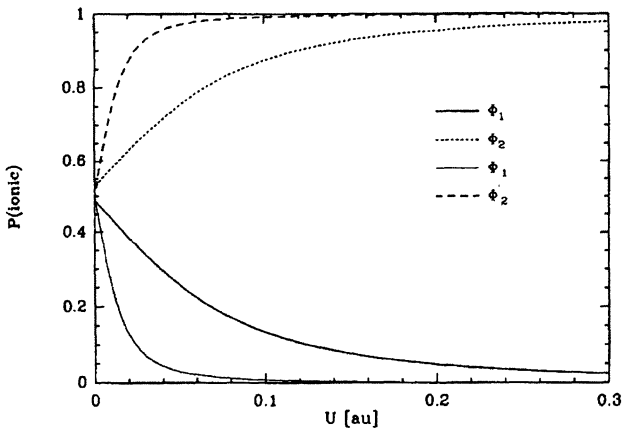


Fig. 2. Probability,  $P(\text{ionic})$ , of an ionic configuration ( $\text{Hg}^+ \text{Hg}^-$ ) for the low lying excited states  $\Phi_1$  and  $\Phi_2$  (see text) in function of the effective Coulomb interaction  $U$

ed state consists mainly of the neutral configuration. Thus the hole in the  $s$ -level and the electron in the  $p$ -level are strongly correlated and nearly always on the same atom.

The peak which is highest in energy corresponds to the transition  $\Phi_0 \rightarrow \Phi_2$ . The energy of this peak increases strongly by 0.12 a.u. when  $U$  increases from 0 to 0.147 a.u. For  $U = 0$  this excited state  $\Phi_2$  consists nearly equal of the ionic and the neutral configurations. For large  $U$ , it consists almost only of the ionic configuration. Thus its energy increases directly with  $U$  and its intensity decreases strongly, because the ground state has only a very small contribution of the ionic configuration for large  $U$ .

The peak in between corresponds to transitions  $\Phi_0 \rightarrow \Phi_1'$  or  $\Phi_0 \rightarrow \Phi_2'$ , which occur for an electric field oriented perpendicularly to the bond. Essentially the same behaviour is observed as for  $\Phi_1$  and  $\Phi_2$ . Note that  $\Phi_1'$  and  $\Phi_2'$  are nearly degenerate for  $U = 0$  and that  $\Phi_2'$  and  $\Phi_2$  are nearly degenerate for larger  $U$ . It is possible that the hopping integrals  $t_{pp\kappa}$  and  $t_{pp\sigma}$  need to be corrected for  $\text{Hg}_n$  and this could result in a change of the splitting of the singlet-singlet absorption line.

Our results for the dynamical polarizability agree qualitatively well with the experiments [1, 5, 6]. If a realistic value for  $U \simeq 0.147$  a.u. is used, then the main absorption lines of  $\text{Hg}_2$  are obtained near the energy of the atomic  $s$ - $p$  transition. In contrast, assuming independent electrons and neglecting correlations, which corresponds to putting  $U = 0$  in our calculation, one would

wrongly obtain several distinct absorption peaks, one of which is almost 0.04 a.u. (1.1 eV) below the energy of the atomic transition.

The static polarizability has also been calculated. It compares quite well at  $U = U(\text{Hg}_2) = 0.147$  a.u. with the experimental result [5], which does not give a significant increase for the static polarizability of the  $\text{Hg}$ -dimer in comparison to single atoms. In our calculation  $\alpha_{av}(\text{Hg}_2)$  increases only approximately 2% with respect to the atomic value in good agreement with the experiment.

## Conclusions

The dynamical and static polarizabilities of the  $\text{Hg}_2$  have been calculated using a Hubbard Hamiltonian including charge fluctuations and the resulting strong electronic correlations. We obtain qualitatively good agreement with the experiment. In contrast, a calculation which neglects charge fluctuations and consequently important electron correlations gives rather different results in strong disagreement with the experiment. It is of interest to extend these calculations to  $\text{Hg}_3$ , etc. and to other clusters like  $\text{Be}_n$ ,  $\text{Mg}_n$ , etc.

Regarding the singlet-triplet optical excitation, we have to add to  $H$  the exchange interaction and the spin-orbit interaction. Due to the spin-orbit interaction one obtains excited states which are a superposition of singlet and triplet states. Then the dipole moment operator acts between the ground state and the excited states modified according to the spin-orbit coupling. Thus, we can obtain within our formalism the singlet-triplet absorption.

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## References

- Schlauf, M., Dimopoulou-Rademann, O., Rademann, K., Even, U., Hensel, F.: *J. Chem. Phys.* **90**, 4630 (1989)
- Pastor, G.M., Stampfli, P., Bennemann, K.H.: *Phys. Scr.* **38**, 623 (1988); *Europhys. Lett.* **7**, 419 (1988)
- Ballone, P., Galli, G.: *Phys. Rev. B* **40**, 8563 (1989)
- Linn, S.H., Liao, C.L., Liao, C.X., Brom Jr. J.M., Ng, C.Y.: *Chem. Phys. Lett.* **105**, 645 (1984)
- Rademann, K., Hensel, F.: (to be published)
- Bréchnignac, C., Broyer, M., Cahuzac, Ph., Delacretaz, G., Labastie, P., Wöste, L.: *Chem. Phys. Lett.* **120**, 559 (1985); *Phys. Rev. Lett.* **60**, 275 (1988)