Theory for Optical Absorption in Small Clusters: Dependence on Atomic Structure and Cluster Size

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We present a theory which permits for the first time a detailed analysis of the dependence of the absorption spectrum on atomic structure and cluster size. Thus, we determine the development of the collective excitations in small clusters and show that their broadening depends sensitively on the atomic structure, in particular at the surface. Results for Hg_n^+ clusters show that the plasmon energy is close to its jellium value in the case of spherical-like structures, but is in general between $\omega_p/\sqrt{3}$ and $\omega_p/\sqrt{2}$ for compact clusters. A particular success of our theory is the identification of the excitations contributing to the absorption peaks.

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The optical absorption of small clusters is one of the most intensively studied problems in cluster physics. However, many questions about the nature of the electronic excitations remain open. In particular, the interplay between single electron-hole and collective excitations and the influence of the atomic structure are still controversial [1,2]. The fact that the plasmon frequencies lie inside the single-particle excitation spectrum makes it difficult to identify the collective excitations and to distinguish them from the electron-hole ones. Note that the usual theories cannot determine explicitly how the collective excitations are composed in terms of single-particle ones and are not applicable for arbitrary cluster structure [1,3]. The jellium model [1], widely used for studying metal clusters, is expected not to be valid in the case of van der Waals and covalent clusters, whose localized valence electrons are more sensitive to changes in the atomic structure.

This and recent experiments [4] suggest that generally the atomic structure of the cluster must be taken into account for studying the electronic excitation spectrum. It is the goal of this paper to present a theory which is valid for a wide range of cluster sizes and atomic structures and which additionally allows us to identify in particular the collective resonances and which single electron-hole excitations contribute to them.

In the absence of an external field we describe the cluster by using a single-particle tight-binding Hamiltonian H_0 with hopping integrals $t_{\gamma\beta}$ between nearest-neighbor (nn) and on-site energies $\epsilon_{l\gamma}$, where l refers to the atomic site and β and γ to the orbital. The interaction of the cluster with an external electromagnetic potential is described as usual by linear response theory [5]. Thus, one finds for the complex susceptibility

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \chi_0(\mathbf{r},\mathbf{r}',\omega) + \int d\mathbf{r}''\, d\mathbf{r}'''\, \chi_0(\mathbf{r},\mathbf{r}'',\omega)\, V(\mathbf{r}'',\mathbf{r}''')\, \chi(\mathbf{r}''',\mathbf{r}',\omega), \tag{1}$$

where $V(\mathbf{r}'',\mathbf{r}''') = e^2/\mid \mathbf{r}-\mathbf{r}' \mid$ is the Coulomb interaction between the electrons. The single-particle susceptibility $\chi_0(\mathbf{r},\mathbf{r}',\omega)$ is expanded in terms of atomiclike Wannier functions $\varphi_{l\beta}(\mathbf{r})$ as

$$\chi_0(\mathbf{r},\mathbf{r}',\omega) = \sum_{\substack{n_1,n_2\\ m_1,m_2}} \chi^0_{n_1n_2m_1m_2}(\omega)\, \varphi^*_{n_1}(\mathbf{r})\, \varphi_{n_2}(\mathbf{r})\, \varphi^*_{m_1}(\mathbf{r}')\, \varphi_{m_2}(\mathbf{r}'). \tag{2}$$

Similarly, one may expand the many-body susceptibility $\chi(\mathbf{r},\mathbf{r}',\omega)$ with coefficients $\chi_{n_1n_2m_1m_2}(\omega)$. Note that the indices n_i and m_i describe site and orbital. For $\chi_{n_1n_2m_1m_2}(\omega)$ one gets clearly, from Eqs. (1) and (2),

$$\chi_{n_1n_2m_1m_2}(\omega) = \chi^0_{n_1n_2m_1m_2}(\omega) + \sum_{j_1,j_2,l_1,l_2} \chi^0_{n_1n_2j_1j_2}(\omega)\, V^{j_1j_2}_{l_1l_2}\, \chi_{l_1l_2m_1m_2}(\omega), \tag{3}$$

with the Coulomb matrix elements $V^{j_1j_2}_{l_1l_2}$. We determine the coefficients $\chi^0_{n_1n_2m_1m_2}(\omega)$ in Eq. (2) by using [5]

$$\chi_0(\mathbf{r},\mathbf{r}',\omega) = \sum_{k,k'} (f_k - f_{k'})\, \frac{\psi^*_k(\mathbf{r})\psi_{k'}(\mathbf{r})\psi^*_k(\mathbf{r}')\psi_{k'}(\mathbf{r}')}{\hbar\omega - (\epsilon_{k'} - \epsilon_k) + i\Gamma}. \tag{4}$$

Diagonalization of the Hamiltonian H_0 yields the energies ϵ_k and the eigenfunctions $\psi_k(\mathbf{r})$, which are expanded in terms of the Wannier functions $\varphi_n(\mathbf{r})$. In Eq. (4) f_k and $f_{k'}$ refer to the Fermi occupation functions. For small clusters the wavelength of the light is always much larger than the cluster size and the polarizability tensor $\alpha_{\mu\nu}(\omega)$ can be written, with the help of the expansion for $\chi(\mathbf{r},\mathbf{r}',\omega)$, as

$$\alpha_{\mu\nu}(\omega) = e^2 \sum_{\substack{i\gamma_1\gamma_2\\ j\beta_1\beta_2}} R^\mu_{i\gamma_1\gamma_2}\, R^\nu_{j\beta_1\beta_2}\, \chi_{i\gamma_1\gamma_2 j\beta_1\beta_2}(\omega), \tag{5}$$

with $R^\mu_{i\gamma_1\gamma_2} = \int d\mathbf{r}\, r_\mu \varphi^*_{i\gamma_1}(\mathbf{r})\varphi_{i\gamma_2}(\mathbf{r})$ and using the approximation $\int d\mathbf{r}\, r_\mu \varphi^*_{i\gamma_1}(\mathbf{r})\varphi_{j\gamma_2}(\mathbf{r}) \simeq 0$ for $i \neq j$. The absorption cross section $\sigma(\omega)$ is given by

$$\sigma(\omega) = \frac{4\pi\omega}{c} \operatorname{Im} \langle \alpha(\omega) \rangle, \tag{6}$$

where c is the velocity of light [6]. Note that $\langle \alpha(\omega) \rangle = \frac{1}{3} \sum_\nu \alpha_{\nu\nu}(\omega)$. If Coulomb interactions are neglected ($V = 0$), one obtains the single-electron absorption cross section $\sigma_0(\omega)$ corresponding to the optical excitations of the tight-binding Hamiltonian H_0.

We have calculated the photoabsorption cross section of various Hg_n^+ clusters having different atomic structures and up to 55 atoms. For the diagonalization of H_0 we use for the singlet-atomic sp gap $\Delta = \epsilon_p - \epsilon_s = 6.7$ eV [7] and $t_{ss} = -t_{sp} = -0.6$ eV, $t_{pp\sigma} = 1.0$ eV, and $t_{pp\pi} = -0.15$ eV for the hopping integrals [8]. Since the Wannier-type wave functions $\varphi_{l\beta}(\mathbf{r})$ are localized around the atoms, the main contribution to the Coulomb interactions $V_{l_1 l_2}^{j_1 j_2}$ is given by one- and two-center integrals. The values for the direct ($U = 7.5$ eV) and the exchange ($C = 1.0$ eV) intra-atomic Coulomb interaction are estimated from atomic data [7]. The interatomic Coulomb integrals are calculated in terms of a multipole expansion up to dipole-dipole interactions [9]. The on-site sp dipole-matrix elements ($R^x_{isp_x} = R^y_{isp_y} = R^z_{isp_z} = 2.85e$ Å) are obtained from the static polarizability of atomic Hg [10]. The nn interatomic distance ($r_0 = 3.36$ Å) is estimated by taking the average of the bulk and dimer values.

In Fig. 1 we show results for the absorption spectrum $\sigma(\omega)$ for different ionized Hg_n^+ clusters and compare them with experimental ones by Haberland *et al.* [11]. Our results referring to $T = 0$ satisfy the usual sum rule for the photoabsorption cross section [6]. In general we find that the optical response depends sensitively on the atomic structure of the cluster. For instance, if we assume a linear cluster structure for very small clusters, we get a dominant peak lying in the gap of the single-particle excitation spectrum $\sigma_0(\omega)$. For compact cluster structures we get more complicated spectra. $\sigma(\omega)$ shows also peaks in the sp gap, but the dominant peak lies at a larger energy, as can be seen in Fig. 1(b) for Hg_5^+ [12]. For clusters with a closed-shell atomic structure like Hg_{13}^+ and Hg_{55}^+ most of the oscillator strength is concentrated on one absorption peak. This seems to be confirmed experimentally for Hg_{13}^+ [see Fig. 1(c)]. The comparison with the experimental results also indicates that the measured Hg_3^+ and Hg_5^+ might have linear structure. Note that the experiments were only performed between 2 eV and 5.9 eV and on warm clusters [11]. The existence of many absorption peaks outside this energy range in our calculated $\sigma(\omega)$ gives an easy explanation for the obvious violation of the sum rule resulting if one uses only the experimental results up to 5.9 eV [11].

We have analyzed the optical absorption spectra of Hg_{13}^+ and Hg_{55}^+ as a function of the different Coulomb integrals. Upon changing only U, $\sigma(\omega)$ remains nearly unaffected. Increasing the dipole-dipole interaction enhances essentially the spectral weight of the dominant peak suggesting that it results from a collective excitation of plasmonic character.

In Fig. 2 we present results for $\sigma(\omega)$ showing the dependence of the absorption spectrum on the electron-

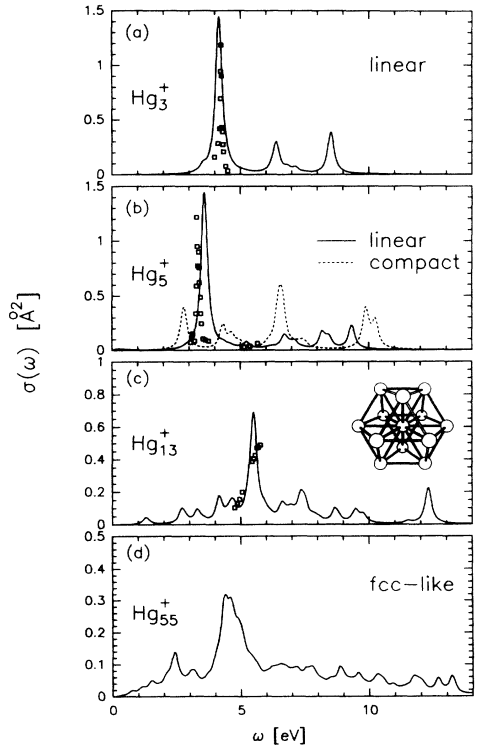

FIG. 1. Calculated photoabsorption cross section $\sigma(\omega)$ (per 6s electron) of Hg_n^+ clusters. The absorption peaks are smoothed using a small damping width $\Gamma = 0.15$ eV. We compare experimental results by Haberland *et al.* (see Ref. [11]).

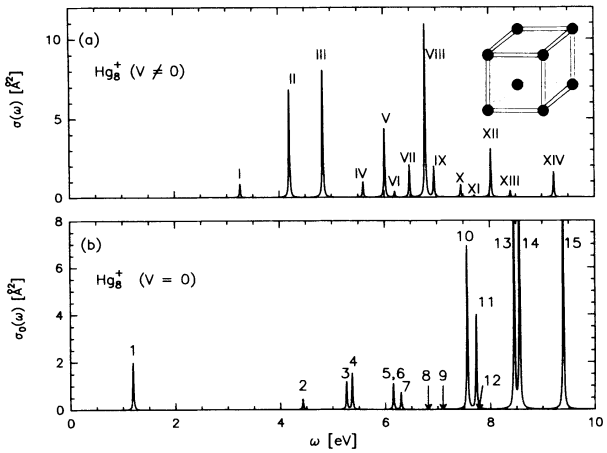

FIG. 2. Dependence of $\sigma(\omega)$ on the interaction V for $\Gamma = 0.01$ eV. Calculated photoabsorption cross section refers to a Hg_8^+ cluster having cubical structure. The optical excitations are labeled with roman and arabic numbers for the many-body and single-particle cases, respectively.

electron interactions V. For the purpose of making the characterization of the spectrum easier we have chosen a small damping parameter Γ and a highly symmetrical Hg_8^+ cluster for which a particular strong collective resonance is expected. Note that the different absorption peaks in $\sigma_0(\omega)$ [Fig. 2(b)] can be clearly related to the single electron-hole excitations ($k \rightarrow k'$). For example, peak 1 is mainly due to $s \rightarrow s$ electron-hole excitations, which are present since in Hg_n^+ the s states are not completely filled. The rest of the spectrum consists mainly of sp excitations. Thus, one can interpret the energy of peak 2 as the single-particle optical sp gap ($\omega_2 \simeq 4.4$ eV). By comparing $\sigma_0(\omega)$ [Fig. 2(b)] with $\sigma(\omega)$ [Fig. 2(a)], one clearly sees that the main effect of the Coulomb interactions results in the appearance of two peaks I and II in the single-particle energy gap and the occurrence of a strong resonance, peak VIII, which dominates the rest of the spectrum.

In Fig. 3 we show results characterizing the composition of the peaks II, VIII, and XIV in Fig. 2(a) in terms of single-particle excitations in order to discriminate collective excitations from single electron-hole ones. For this analysis we present a method based only on the properties of the susceptibility $\chi(\mathbf{r},\mathbf{r}',\omega)$. We expand the susceptibilities $\chi_0(\mathbf{r},\mathbf{r}',\omega)$ and $\chi(\mathbf{r},\mathbf{r}',\omega)$ in terms of the eigenfunctions of H_0 with coefficients $\Lambda^0_{kk'k_1k_1'}(\omega)$ and $\Lambda_{kk'k_1k_1'}(\omega)$. Thus, with the help of Eq. (4) one obtains

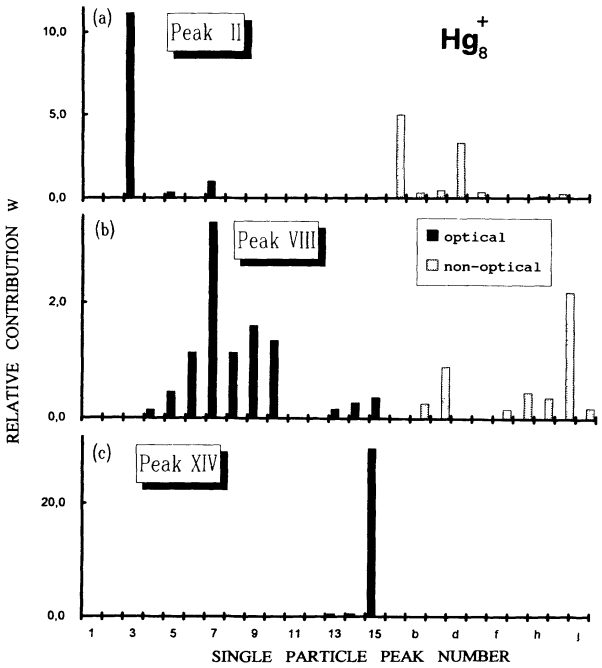

FIG. 3. Relative contribution $W^M_{kk'}$ of the single-particle electron-hole excitations (optical and nonoptical) to different many-body optical excitations in cubic Hg_8^+. This shows how the single electron-hole excitations contribute to the absorption peaks (a) II, (b) VIII, and, (c) XIV of the spectrum shown in Fig. 2(a).

$$\lim_{\Gamma\to 0} \mathrm{Im}\,\Lambda^0_{kk'k_1k_1'}(\omega) = -\frac{1}{\pi}\sum_{q,q'} (f_q - f_{q'})\,\delta(\omega-\omega_{qq'}) \times \delta_{kq}\,\delta_{k'q}\,\delta_{k_1q'}\,\delta_{k_1'q'}, \quad (7)$$

where $\hbar\omega_{qq'} = \epsilon_{q'} - \epsilon_q$ is the energy corresponding to a single-particle excitation $q \rightarrow q'$ contributing to a peak in the single-particle spectrum $\sigma_0(\omega)$. Now, we can define the function

$$A^M_{kk'} = \lim_{\Gamma\to 0} \mathrm{Im}\,\Lambda_{kk'kk'}(\omega_M), \quad (8)$$

where ω_M is the energy of the Mth absorption peak in the spectrum $\sigma(\omega)$ including many-body interactions. Thus, the normalized factor $W^M_{kk'} = A^M_{kk'}/\sum_{qq'} A^M_{qq'}$ are the relative contribution of a single-particle excitation $k \rightarrow k'$, resulting from H_0, to the many-body peak M and can be used to distinguish between single-particle and collective excitations. For a peak due to a single electron-hole excitation one gets only one $W^M_{kk'} \neq 0$, whereas a collective resonance is characterized by many nonzero $W^M_{kk'}$'s. Since our method is based on $\chi(\mathbf{r},\mathbf{r}',\omega)$, we can determine the contributions of optical as well as nonoptical excitations.

The results in Fig. 3 illustrate $W^M_{kk'}$ for three different many-body peaks M in $\sigma(\omega)$ of Hg_8^+. To the peak II, lying in the sp gap at 4.2 eV, mainly three single-particle excitations contribute [see Fig. 3(a)]. These electron-hole excitations have energies only slightly larger than the sp gap energy. As a consequence, we may interpret peak II as an excitoniclike excitation. Perhaps even more interesting is the composition of the dominating peak VIII. As can be seen in Fig. 3(b), almost all single-particle peaks participate in this resonance at $\omega_8^s(\text{cube}) = 6.8$ eV. We conclude that this is a plasmonlike collective excitation. Note that its energy is larger than the classical Mie value $\omega_p/\sqrt{3} = 6.3$ eV. It can be seen from Fig. 3(c) that the Coulomb interactions in small clusters not only produce excitoniclike and plasmonlike resonances, but also leave some electron-hole excitations unchanged or just shift their energies, as is the case in solid state physics. The peak XIV in Fig. 3(c) is due to the same electron-hole excitation as the single-particle peak 15 in $\sigma_0(\omega)$ [Fig. 2(b)]. The Coulomb interactions cause only a redshift of 0.2 eV of the position of the peak.

By analyzing in the same way the spectra of Hg_3^+ and Hg_5^+ for different atomic structures, we have found that the dominant peaks in the linear structures are presumably of excitonic character. In contrast, the dominant peak in the compact structure of Hg_5^+ is a collective mode with plasmonic character, to which almost all single-particle excitations contribute. Thus, the main effect of the linear structure is to suppress the optical collective modes, whereas the compact structures favor them. Futhermore, we can also conclude that the dominant absorption peaks in Hg_{13}^+ and Hg_{55}^+ [Figs. 1(c) and 1(d)] correspond to collective excitations. These are redshifted with respect to the classical surface plasmon

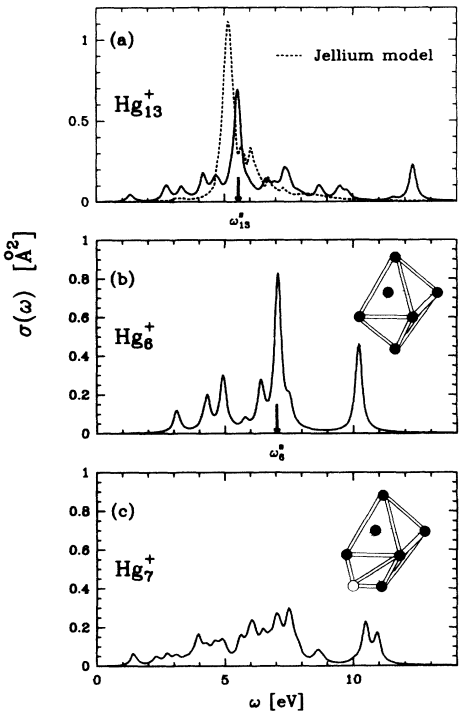

FIG. 4. Calculated photoabsorption cross section of Hg_n^+ clusters. ω_n^s refers to the frequency of the collective resonances. For comparison we also show results obtained by using a spherical-like jellium model. This demonstrates the sensitive dependence of $\sigma(\omega)$ on the atomic structure of the cluster surface. Note that the additional atom in Hg_7^+ is indicated.

frequency $\omega_p/\sqrt{3}$ [13].

The interpretation of the collective optical excitation in the optical spectrum of Hg_{13}^+ as a surface plasmon becomes even more evident if we compare our absorption spectra $\sigma(\omega)$ with results obtained by us using the jellium model [14]. Both spectra shown in Fig. 4(a) are similar, and the corresponding dominating peaks are very close to each other. This agreement of the large plasmonlike peaks results from the fact that the fcc structure of Hg_{13}^+ is approximately spherical-like and therefore similar to the spherical jellium background. Note the jellium surface plasmon is, however, more redshifted with respect to $\omega_p/\sqrt{3}$ and to the experimental results [11]. Apart from the plasmonlike excitation, the jellium model shows a relatively poor structured spectrum with almost no other absorption peaks. This demonstrates that the richness of our calculated spectrum is due to the atomic structure. Not only the electron-hole excitations depend on the atomic structure, but also the exact energy of the surface plasmon. By comparing the plasmonlike frequencies of spherical-like Hg_{13}^+ and cubical Hg_8^+ we obtain approximately $\omega_8^s(\text{cube})/\omega_{13}^s(\text{fcc}) \simeq \sqrt{3}/\sqrt{2}$, which is the classical relation between the surface plasmon frequencies of a plane and a sphere. This shows clearly the sensitivity with respect to the cluster surface. Furthermore, we have calculated $\sigma(\omega)$ for nonsymmetric cluster shapes, as, for example, the fcc-like Hg_{20}^+. We obtain a broadening of the whole spectrum and particularly a Landau damping of the collective excitations. The plasmon resonance always occurs between the two "limits" ω_{13}^s(fcc) and ω_8^s(cube). To demonstrate how dramatically the absorption spectra are affected by surface changes of the cluster, we show in Figs. 4(b) and 4(c) the calculated absorption cross sections for a symmetric cluster structure (Hg_6^+) and for the same structure with an additional atom at the surface (Hg_7^+), which destroys the symmetry of the Hg_6^+ structure and induces a strong broadening of the plasmon and other collective excitations. Such a broadening of the collective resonances due to surface perturbations have been recently observed in optical experiments on Au_{55} clusters [4].

Summarizing, we have developed a theory which can be used to calculate optical response of clusters with arbitrary cluster structure. We have analyzed for the first time the broadening of the collective excitations upon structural changes. We presented a method for characterizing the optical excitations. The results should be of general validity and our theory should apply to clusters in matrices and to surface physics.

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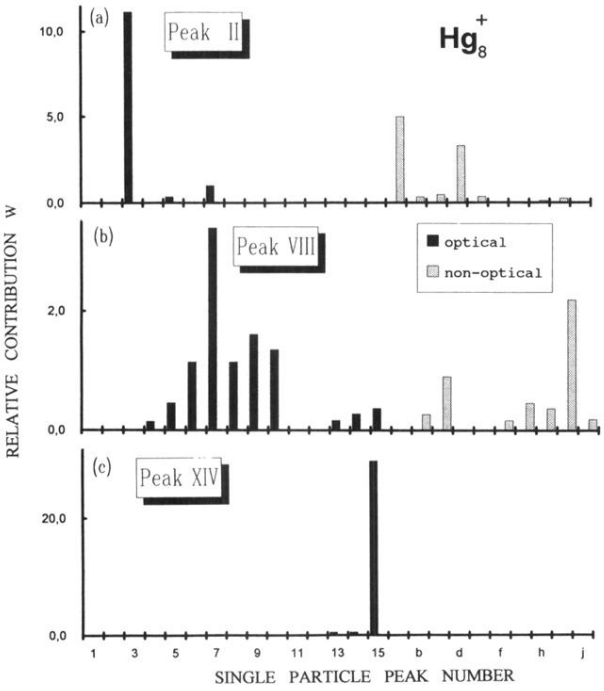

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