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Medium-induced change of the optical response of metal clusters in rare-gas matrices

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Interaction with the surrounding medium modifies the optical response of embedded metal clusters. For clusters from about ten to a few hundreds of silver atoms, embedded in rare-gas matrices, we study the environment effect within the matrix random phase approximation with exact exchange (RPAE) quantum approach, which has proved successful for free silver clusters. The polarizable surrounding medium screens the residual two-body RPAE interaction, adds a polarization term to the one-body potential, and shifts the vacuum energy of the active delocalized valence electrons. Within this model, we calculate the dipole oscillator strength distribution for Ag clusters embedded in helium droplets, neon, argon, krypton, and xenon matrices. The main contribution to the dipole surface plasmon red shift originates from the rare-gas polarization screening of the two-body interaction. The large size limit of the dipole surface plasmon agrees well with the classical prediction.

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I. INTRODUCTION

Most often, experimental photoabsorption studies of metal clusters are carried out on clusters embedded in matrices in order to have a high density, a well-defined temperature, and a cage effect to prevent fragmentation. Rare-gas matrices are preferred in order to mitigate the interaction with the nanoparticle and reach its intrinsic optical properties. For a classical spherical metallic particle of radius R embedded in a continuous medium with a dielectric constant ϵ_m , the absorption cross section at frequency ω is given by

$$\sigma(\omega) = \frac{4\pi\omega R^3 \sqrt{\epsilon_m}}{c} \text{Im} \frac{\epsilon(\omega) - \epsilon_m}{\epsilon(\omega) + 2\epsilon_m}, \quad (1)$$

where $\epsilon(\omega)$ is the dielectric function of the nanoparticle material. Early experiments on silver clusters ($10 < R < 100 \text{ \AA}$) embedded in an argon matrix [1] revealed a blue shift of the dipolar surface plasmon resonance as the cluster size decreased. Measured photoabsorption spectra of very small Ag_n clusters ($n = 2\text{--}39$) embedded in rare-gas matrices [2,3] were explained by the classical Mie theory with a two-region dielectric function designed for an embedded core-shell system. In the core region, a bulk dielectric function was used, while the Drude dielectric function was used in the intermediate region. This core-shell model reproduced reasonably well the size dependence of the measured photoabsorption spectra [1,3]. Other authors have employed similar classical approaches to the optical response of embedded noble-metal clusters [4,5].

Optical absorption spectra for silver clusters embedded in helium nanodroplets have been reported too [6–10]. In particular, the very precise measurements for Ag_8 [6,7] deserve special attention as the experiments showed a single narrow peak of width about 60 meV. Coupled cluster calculations with an 11-electron relativistic effective core potential on free pure Ag_8 (T_d symmetry) showed satellite peaks in addition to a strong peak which was blue shifted with respect

to the experimental (helium-embedded) peak [11]. Further calculations using time-dependent density functional theory (TDDFT) on real time and real space predicted an optical spectrum in quite good agreement with the experimental one, by again neglecting the environment effect [12]. Optical spectra of small silver clusters embedded in a neon matrix and in an argon matrix were measured and calculated using time-dependent density functional theory (TDDFT) while neglecting the matrix effects [13,14]. Clearly, advanced quantum calculations taking into account the medium effects remain challenging. In a pioneering jellium time-dependent local density approximation (TDLDA) quantum description of the cluster-matrix interaction applied to sodium, potassium, and silver clusters, Rubio and Serra replaced the direct Coulomb electron-electron interaction term with a screened Coulomb interaction as obtained for a classical metal sphere embedded into an infinite dielectric medium [15], while the exchange-correlation term and the electron-ion interaction were not changed. They found a medium-matrix-induced red shift which typically was smaller than predicted later by Kurkina and Farberovich, who also used the TDLDA method with a medium-corrected-polarization potential [16]. Later, Gross *et al.* addressed the issue for argon-embedded sodium atoms and sodium dimers [17] by considering both the metal atom core and argon atom as polarizable dipoles. They found a red shift of the oscillator strength for sodium dimers, while a blue shift was predicted for single sodium atoms. Note that their calculation was limited to sodium dimers by the high computation cost of the configuration interaction method that they used. In 2004, Gervais *et al.* implemented the Gross's cluster-matrix polarization interaction into TDDFT and calculated the optical response of $\text{Na}_{2,4,8}$ embedded in up to 1396 argon atoms [18,19]. A significant change on the absorption spectrum was found for Na_4 due to the argon matrix, while a very slight shift for Na_8 was predicted. Moreover, the authors concluded that the optical response of embedded sodium clusters depended on the details of the matrix configuration [18,19]. Later, a conductorlike screening model of the solvation model was implemented in TDDFT and showed that the argon matrix shifts the optical spectra of

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silver clusters to lower energy by about 0.17 eV [20], which is in the same direction as the experimental estimated value of 0.24 eV [3]. As for noble-metal clusters (of size up to about a thousand atoms) embedded in various matrices, Lermé and his collaborators conducted a detailed analysis of the red shift and profile of the optical absorption spectrum, within a hybrid approach based on classical concepts for the dielectric medium effects and TDLDA [21–23].

In order to have a comprehensive understanding of the optical response of both free and embedded metal clusters, here we revisit the problem from the modified random phase approximation with exact exchange (RPAE) perspective, treating the polarization by the embedding rare-gas medium and that by the silver core on equal footing. We would like to emphasize that since helium atoms have a very small dipole polarizability, the medium-polarization correction will be negligible. Nevertheless, the energy barrier due to the strong repulsion by helium 1s core electrons will be the dominating effect [24,25]. Section II presents our matrix-polarization-corrected model Hamiltonian for the delocalized valence electrons in silver metal clusters. We calculate the oscillator strength distribution in the framework of the previously proposed core-polarization-corrected RPAE approach [26]. In Sec. III, numerical results are presented for Ag_n clusters with closed shell number of electrons ($n = 8, 20, 58, 92, 138, 198$) embedded in He, Ne, Ar, Kr, and Xe matrices. A significant red shift of the oscillator strength peak was found due to matrix screening on the dipole term of the two-body Coulomb interaction. The large cluster limit of the red shift agrees with the classical electromagnetic prediction. An atomic system of units ($\hbar = e = m_e = 4\pi\epsilon_0 = 1$) is used throughout the paper.

II. MODEL

Consider a cluster of N metal atoms of radius R_J embedded in a rare-gas (Ne, Ar, Kr, Xe) matrix. For simple alkali-metal clusters, a pure jellium model (JM) with fully delocalized valence electrons can be used with confidence. For the silver clusters of present interest, we adopt the core-polarization correction introduced in our previous work [26] to model a modified jellium Hamiltonian for the interacting 5s valence electrons. For embedded clusters, the Hamiltonian has a similar structure and can be written as

$$H = \sum_i \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i < j} u_{\text{cp}}(\mathbf{r}_i, \mathbf{r}_j) + \sum_i V_{\text{JM}}(\mathbf{r}_i) + \sum_i V_{\text{cp}}(\mathbf{r}_i) + \sum_i V_0(\mathbf{r}_i). \quad (2)$$

The term u_{cp} accounts for the screening of the two-body interaction by both the silver atom core electrons (mainly 4d) and the embedding medium. There is a correction of the same causes to the one-body term, V_{cp} , which adds to the jellium ionic Coulomb potential V_{JM} . Since the valence electrons of the metal cluster are treated as free electrons which can spill out and the rare gas is an infinite media, the vacuum zero point shall be corrected by an energy barrier V_0 coming from the conduction-band minimum of the rare-gas matrix. V_0 is the energy of the bottom band relative to the vacuum level. It has been measured by the difference of the work function in the

liquid from that in the vacuum [24,27,28]. For helium, V_0 is positive as expected from Pauli repulsion. For free clusters, as discussed in our previous work [26], $V_0 = 0$ and the two-body and one-body corrections are

$$u_{\text{cp}}(\mathbf{r}_i, \mathbf{r}_j) = -\frac{4\pi}{3} R_J^3 \alpha_I n_I f(\mathbf{r}_i) f(\mathbf{r}_j), \quad (3)$$

$$f(\mathbf{r}) = \begin{cases} \frac{r}{R_J^3} & \text{if } r < R_J \\ \frac{R_J}{r^3} & \text{if } r > R_J, \end{cases}$$

$$V_{\text{cp}}(\mathbf{r}) = -\frac{2\pi}{3} R_J^3 \alpha_I n_I f^2(\mathbf{r}), \quad (4)$$

where α_I is the dipole polarizability of silver cations in the jellium and n_I is the density ($N = \frac{4\pi}{3} R_J^3 n_I$).

The polarization effect from the surrounding rare-gas medium characterized by atomic polarizability α_m and density of atoms n_m can be treated in the same way, which leads to a two-body correction,

$$u_{\text{cp}}(\mathbf{r}_i, \mathbf{r}_j) = -\alpha_I n_I \int_0^{R_J} d\mathbf{R} \gamma(\mathbf{R}) \frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3} \frac{\mathbf{R} - \mathbf{r}_j}{|\mathbf{R} - \mathbf{r}_j|^3} - \alpha_m n_m \int_{R_J}^{\infty} d\mathbf{R} \gamma(\mathbf{R}) \frac{\mathbf{R} - \mathbf{r}_i}{|\mathbf{R} - \mathbf{r}_i|^3} \frac{\mathbf{R} - \mathbf{r}_j}{|\mathbf{R} - \mathbf{r}_j|^3}, \quad (5)$$

where we have taken into account the local field corrections $\gamma(\mathbf{R})$. The local field at position P is

$$\mathbf{E}_{\text{loc}}(P) = \gamma(P) \mathbf{E}(P) = \mathbf{E}(P) + \sum_M \gamma(M) \mathbf{E}_M^{\text{dip}}(P), \quad (6)$$

where $\mathbf{E}_M^{\text{dip}}(P)$ is the electric field created by the induced dipole at position M . For a uniform structure-less medium with atomic polarizability α and density n , the local field correction factor fulfills the self-consistent relation [29]

$$\gamma(\mathbf{R}) = 1 - \frac{8\pi n}{3} \alpha \gamma(\mathbf{R}), \quad (7)$$

which leads to the well-known Lorentz local field factor

$$\gamma = 1/(1 + 2\alpha^*), \quad (8)$$

where $\alpha^* = \frac{4\pi n}{3} \alpha$. For the present problem, the cluster is viewed as a polarizable particle of polarizability $N\alpha_I$. When embedded, the local field factor γ^I will be

$$\gamma^I = 1 - 2\alpha_m^* \gamma^m. \quad (9)$$

Next, we need to define γ^m . Because of breaking translational symmetry, it should be position dependent. However, due to the facts that far away from the cluster there is no induced dipole because the cluster is neutral and that the dipole transition density is peaked on the surface [30], we will assume γ^m to be constant and calculated on the cluster surface. Following Lekner [29] exactly, we arrive at

$$\gamma^m = 1 - \alpha_I^* \gamma^I - \alpha_m^* \gamma^m. \quad (10)$$

Solving the above two equations and applying the Clausius-Mossotti (CM) relation, we obtain

$$\gamma^m = \frac{1 - \alpha_I^*}{1 - 2\alpha_I^* \alpha_m^* + \alpha_m^*} = \frac{\epsilon_m + 2}{\epsilon_I + 2\epsilon_m}, \quad (11)$$

$$\gamma^I = \frac{1 - \alpha_m^*}{1 - 2\alpha_I^* \alpha_m^* + \alpha_m^*} = \frac{\epsilon_I + 2}{\epsilon_I + 2\epsilon_m}. \quad (12)$$

Restricting to the dipole approximation in Eq. (5), the two-body correction reads

$$u_{\text{cp}}^{L=1}(\mathbf{r}_i, \mathbf{r}_j) \approx -(\alpha_I^* \gamma^I + 2\alpha_m^* \gamma^m) R_J^3 f(\mathbf{r}_i) f(\mathbf{r}_j). \quad (13)$$

It is then straightforward to obtain the one-body correction V_{cp} by setting $\mathbf{r}_i = \mathbf{r}_j$ in the two-body correction. Solving the matrix random phase approximation with exact exchange equation, one obtains dipole excitation energies ω_k and dipole oscillator strength distribution f_k . The numerical calculation exactly follows our previous work [26]. Note that the two-body correction can be seen as a screening effect on the dipole term of the pure Coulomb interaction. One obtains the factor β for the screening,

$$V^{L=1} = \left[\frac{r_{<}}{r_{>}^2} - (\alpha_I^* \gamma^I + 2\alpha_m^* \gamma^m) R_J^3 f(r_{<}) f(r_{>}) \right]$$

$$\cos(\theta_{\mathbf{r}_{<}, \mathbf{r}_{>}}) = \beta V_{\text{Coulomb}}^{L=1}. \quad (14)$$

In the large size limit ($r_{<} \approx r_{>} \approx R_J$), using Eqs. (11) and (12), one obtains

$$\beta \approx \frac{3}{\epsilon_I + 2\epsilon_m}. \quad (15)$$

Thus, in this limit, the medium and silver core screening effects lead to an effective electron charge $e^* = \sqrt{\beta}$ and,

consequently, change the pure jellium Mie frequency $\omega_M = \sqrt{\frac{4\pi n_I e^2}{3m_e}}$ to

$$\omega_M^* = \omega_M \sqrt{\frac{3}{\epsilon_I + 2\epsilon_m}}. \quad (16)$$

Classically, for a metal cluster with dielectric function $\epsilon(\omega) = \epsilon_I - \omega_p^2/\omega^2$ [31] embedded in a rare-gas matrix with dielectric constant of ϵ_m , the absorption cross section is given by Eq. (1). The surface plasmon frequency reads [32]

$$\omega_{\text{sp}} = \omega_M \sqrt{\frac{3}{\epsilon_I + 2\epsilon_m}}. \quad (17)$$

We conclude that our model agrees with the classical prediction in the large size limit.

III. RESULTS AND DISCUSSION

The matrix-polarization-corrected Hamiltonian [Eq. (2)] was implemented into the Hartree-Fock and RPAE codes, as discussed in our previous work [26].

Table I gives the parameters related to the rare-gas embedding medium: its density, atomic polarizability (taken from Ref. [33]) with corresponding dielectric constant obtained

FIG. 1. Oscillator strength distribution of free and embedded (He, Ne, Ar, Kr, and Xe) silver clusters ($\text{Ag}_{8,20,58,92,138,198}$) as a function of dipole transition energy (eV).

TABLE I. Parameters for He, Ne, Ar, Kr, and Xe embedding media. n is the density. α is the dipole polarizability of rare-gas atoms taken from Ref. [33]. ϵ is the dielectric constant. V_0 is the conduction-band minimum of the rare-gas medium.

Element	$10^3 n$ (a.u.)	α (a.u.)	ϵ	V_0 (eV)
He				+1.04 (Theor. [34]) +1.3 (Expt. [27])
Ne	6.64	2.67	1.24	+1.1 (Expt. [35])
Ar	3.73	10.77	1.61	+0.3 (Expt. [35])
Kr	3.22	16.47	1.86	-0.25 (Expt. [35])
Xe	2.45	26.97	2.15	-0.46 (Expt. [35])

from the CM relation, and conduction-band minimum V_0 taken from Refs. [27,34,35]. As discussed before, we neglected the polarization effect of He since it has a very small dipole polarizability.

Figure 1 shows the oscillator strength distribution for Ag_N with $N = 8, 20, 58, 92, 138, 198$ embedded in helium, neon, argon, krypton, and xenon. Compared with free clusters, the oscillator strength distribution of silver clusters embedded in helium slightly shifts to higher energy as a result of the repulsive energy coming from the positive conduction-band minimum. The magnitude of this effect decreases as the cluster size increases. From the green and black lines of Fig. 2, one can clearly see that the large size limit is unchanged by the He medium, which is V_0 . Another trend shown in Fig. 1 is that as the media dielectric constant increases, the oscillator strength distribution shifts to lower energy and presents a narrower pattern. This is due to the polarization effect of the rare-gas medium which reinforces the screening of the dipole term of the Coulomb interaction (more detailed discussion on the polarization effect can be found in [26]).

Figure 2 shows the size evolution of the dipole mean energy, as predicted by the present theoretical model. The lines are a linear fit for Ag_N with $N = 58, 92, 138, 198$. The large

FIG. 2. Model-predicted evolution of the surface plasmon peak (mean energy) as a function of the inverse radius of silver clusters of N silver atoms embedded in rare-gas medium. The straight lines are the least-squares fitting for $N = 198, 138, 92, 58$. Black: no medium. Green, red, blue, magenta, and yellow: clusters embedded in He, Ne, Ar, Kr, and Xe, respectively.

TABLE II. Calculated and classical [Eq. (17)] surface plasmon peak position (eV).

Medium	Free	He	Ne	Ar	Kr	Xe
Calculation (Fig. 2)	3.95	3.95	3.78	3.56	3.43	3.30
ω_{sp} [Eq. (17)]	3.98	3.98	3.81	3.58	3.44	3.31

size limits are indicated by the black bars on the energy axis. Systematically, the $1/R$ linear behavior works well only for radii larger than about 6 Å. For smaller radii, i.e., number of atoms smaller than 50, the mean energy does not depend much on size and is sensitive to the details of the oscillator strength distribution arising from the quantum confinement.

Table II gives the large size limits from the linear fitting of Fig. 2 and the classical predictions from Eq. (17). The comparison between these values demonstrates that our model will reproduce the classical limit and that the energy barrier V_0 only affects the surface plasmon in small clusters. The large cluster limit is independent of V_0 and is shifted by polarization effects only.

Figure 3 compares our theoretical predictions with the experimental optical absorption spectra of $\text{Ag}_{20,58,92}$ in Ne matrices, as reported by Yu [36]. This author only provided Lorentzian shapes that were fitted to the experimental data. Our model predictions appear as lines of the dipole oscillator strength distribution. One can observe a very nice agreement between theory and experimental data. For these medium-size clusters embedded in neon, the oscillator strength distribution is a delicate balance between polarization effects and the barrier V_0 .

FIG. 3. Model-predicted dipole oscillator strength of silver clusters (Ag_{20} , Ag_{58} , and Ag_{92}) embedded in the Ne matrix. The continuous lines are fitting curves to the experimental data [36].

FIG. 4. Model-predicted dipole oscillator strength of a Ag_8 cluster embedded in helium liquid for three different values of V_0 (see Table I). Scattered dots are experimental results from [7].

The optical spectrum of Ag_8 in a helium droplet was measured by two groups [6,7] with different experimental methods. Within the approximation level of the present work of concern, both experimental spectra are similar and typically show a very narrow distribution peaked at 311 nm. Figure 4 compares our calculated optical spectrum with different values of the barrier V_0 with the experimental spectrum measured by Diederich *et al.* [7]. Both spectra peak at the same wavelength when we assume the barrier to be $V_0 = 1.3$ eV, which indeed is the value measured by Sommer [27]. For $V_0 = 0$, which is a free cluster, the resonance is at 340 nm. Thus, we conclude that the helium environment causes a significant blue shift of about 0.34 eV for small clusters.

IV. CONCLUSION

The optical response of embedded metal clusters has been described by a polarization-corrected jellium model with a energy barrier coming from the medium conduction-band minimum. The polarization energy term enters the Hamiltonian of the metal valence electrons, which further leads to a two-body dipole interaction and a one-body self-energy potential. The two-body term can be viewed as a size-independent screening on the dipole component of Coulomb interaction. The one-body term, however, decreases as cluster size increases. The energy barrier effect is negligible for large clusters. When the dipole polarizability of a rare-gas atom goes to zero with no energy barrier, the formalism is exactly that worked out in our previous paper [26]. Calculations on Ag clusters embedded in Ne, Ar, Kr, and Xe matrices were done. The predicted red shift with increasing size depends strongly on the embedding rare gas. Indeed, larger rare gas with larger dielectric constants induces a stronger polarization screening on the dipole term of the Coulomb interaction. The large size limit of the surface plasmon peak predicted by our model agrees well with classical theory. Good agreement between the oscillator strength distribution calculated by our model and the experimentally measured optical spectrum of $\text{Ag}_{20,58,92}$ embedded in the Ne matrix is found, which demonstrates that for a medium-size cluster, the polarization effect, finite quantum effects, and energy barrier are important. For an He droplet, we only take into account the energy barrier while neglecting the polarization effect since He has a rather small polarizability. The experimental value of $V_0 = 1.3$ eV for the barrier reproduces the optical spectrum of Ag_8 in the He droplet quite well.

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