

SUPPLEMENTARY MATERIAL

Here we elaborate on our equilibrium and time dependent DFT calculations.

A. The electronic structure calculation

The electronic structure for the metallic dimers was computed with a jellium pseudo-potential. For a metallic structure of given shape and volume, the jellium pseudo-potential is chosen as constant V_0 inside that volume and zero outside. The value of $V_0 = -0.1$ Hartree was chosen so that the Fermi level of the electrons is 4.0 eV below the vacuum level. The Fermi level is computed by requiring that the number of electrons be equal to vol/v_s , with the radius of the Wigner-Seitz sphere v_s taken as $r_s = 3.0$ Bohr.

Due to the cylindrical symmetry of the system, the Kohn-Sham orbitals can be written as $\psi_{nm}(\rho, z)e^{im\phi}$, where $\psi_{nm}(\rho, z)$ satisfy the reduced self-consistent Kohn-Sham equations (in units $m = \hbar = e = 1$):

$$\left(-\frac{1}{2} \frac{\partial^2}{\partial \rho^2} - \frac{1}{2} \frac{\partial^2}{\partial z^2} + \frac{m^2 - 1/4}{2\rho^2} + V_{\text{eff}} \right) \psi_{nm} = \epsilon_{nm} \psi_{nm}. \quad (1)$$

Here, $V_{\text{eff}}[n]$ includes the jellium pseudo-potential, the Hartree and exchange-correlation potentials:

$$V_{\text{eff}}[n] = V_0 + v_H[n - n_0] + v_{\text{XC}}[n]. \quad (2)$$

Here, n_0 is the positive pseudo-ionic charge, which in the jellium approximation is a uniform density of $1/v_s$. For the exchange-correlation part, we use the LDA version of Ref.¹. The electron density was calculated from:

$$n(\rho, z) = \sum_{n,m} \frac{|\psi_{nm}(\rho, z)|^2}{1 + e^{\beta(\epsilon_{nm} - \epsilon_F)}}, \quad (3)$$

where $\beta = 1/kT$ was chosen much smaller than the typical energy level spacings seen during the calculations. The terms for which $1/(1 + e^{\beta(\epsilon_{nm} - \mu)}) < 10^{-8}$ are discarded in the above summation.

The reduced Kohn-Sham equations were implemented using a standard finite differences approach in 2 dimensions, with special care given to the boundary conditions at $\rho = 0$, where the centrifugal potential becomes extremely singular. The Hartree potential is computed directly from the Poisson equation: $\nabla^2 v_H = 4\pi(n - n_0)$. The electronic structure code was tested on several systems where the exact solution is known.

B. The Optical Absorption Calculation

The frequency dependent optical absorption calculation was completed within the Time Dependent Adiabatic Local Density Approximation (TDLDA) framework. The linear response equation for the frequency

dependent density perturbation Δn is given by:

$$\Delta n(\vec{r}, \omega) = \int d\vec{r}' \chi^0(\vec{r}, \vec{r}'; \omega) \times \left[v_0(\vec{r}', \omega) + \frac{\delta V_{\text{eff}}}{\delta n} \Delta n(\vec{r}', \omega) \right], \quad (4)$$

where V_{eff} is the same effective potential appearing in the equilibrium electronic structure calculation and $v_0(\vec{r}, \omega)$ is the external driving potential. In the dipole approximation, $v_0(\vec{r}, t) = \vec{E}_0 \cdot \vec{r} e^{i\omega t}$. From the perturbed density we compute the induced dipole moment $\vec{P}(\omega) = \int \vec{r} \Delta n(\vec{r}, \omega) d^3\vec{r}$. In the linear response regime, $\vec{P}(\omega)$ is proportional to the driving field \vec{E}_0 : $\vec{P}(\omega) = \hat{\alpha}(\omega) \vec{E}_0$, where $\hat{\alpha}(\omega)$ is the frequency dependent polarizability tensor of the system. The total optical absorption cross section $\sigma(\omega)$ is directly related to the imaginary part of the polarizability. For a driving field oriented along the z direction, $\sigma(\omega) = \frac{4\pi}{c} \text{Im}[\alpha_{zz}(\omega)]$.

The independent-electron density-density correlation function $\chi^0(\vec{r}, \vec{r}'; \omega)$ can be computed using a Green's function expansion:²

$$\chi^0(\vec{r}, \vec{r}'; \omega) = \sum_i f_i [\phi_i(\vec{r}') \phi_i^*(\vec{r}) G(\vec{r}, \vec{r}'; \epsilon_i + \hbar\omega + i\delta) + \phi_i^*(\vec{r}') \phi_i(\vec{r}) G(\vec{r}', \vec{r}; \epsilon_i - \hbar\omega - i\delta)], \quad (5)$$

where $\{\phi, \epsilon_i\}$ are the Kohn-Sham orbitals and the corresponding energies, $G(\vec{r}, \vec{r}', \epsilon)$ is the Green's function for the Kohn-Sham Hamiltonian and f_i 's are the finite temperature occupation numbers.

Due to the cylindrical symmetry, the Green's function and the independent-electron response function factorize as

$$G(\vec{r}, \vec{r}'; \epsilon) = \sum_M G_M(\rho, z, \rho', z'; \epsilon) e^{-iM(\phi - \phi')} \quad (6)$$

$$\chi^0(\vec{r}, \vec{r}'; \omega) = \sum_M \chi_M^0(\rho, z, \rho', z'; \omega) e^{iM(\phi - \phi')}$$

with

$$\chi_M^0 = \frac{1}{2\pi} \sum_{n,m} f_{nm} \psi_{nm}(\rho, z) \psi_{nm}(\rho', z') \times \left[G_{M-m}(\rho, z, \rho', z'; \epsilon_{nm} + \hbar\omega + i\delta) + G_{M-m}(\rho, z, \rho', z'; \epsilon_{nm} - \hbar\omega - i\delta) \right]. \quad (7)$$

The self-consistent equation for Δn is a linear equation, which can be written in an operator form as

$$[I - \hat{\chi}^0 * \delta_n V_{\text{eff}}] \Delta n = \hat{\chi}^0 v_0. \quad (8)$$

We use the Biconjugate Gradient Algorithm³ to solve this linear equation. Note that we use the Biconjugate and not the simpler Conjugate Algorithm since the operator multiplying Δn is not symmetric. In this algorithm, the

only thing that we need to supply is an efficient subroutine that applies $\hat{\chi}^0$ on a general function $V(\rho, z)$. The action of $\delta V_{\text{eff}}/\delta n$ is trivial to compute.

In the following we elaborate on how we constructed this subroutine. We consider the case when the field E_0 is oriented along the symmetry axis of the system, in which case we can restrict to the sector $M = 0$. We have:

$$\begin{aligned} (\hat{\chi}_{M=0}^0 V)(\rho, z) &= \sum_{n,m} f_{nm} \psi_{nm}(\rho, z) \\ &\times \int d\rho' dz' \left[G_m(\rho, z, \rho', z'; \epsilon_{nm} + \hbar\omega + i\delta) \right. \\ &\left. + G_m(\rho, z, \rho', z'; \epsilon_{nm} - \hbar\omega - i\delta) \right] \psi_{nm}(\rho', z') V(\rho', z'). \end{aligned} \quad (9)$$

Note that we used G_m instead of G_{-m} because the reduced Kohn-Sham Hamiltonian depends only on m^2 . Now, the key observation is that the above integral is equal to

$$U_{nm}^+(\rho, z; \omega) + U_{nm}^-(\rho, z; \omega), \quad (10)$$

where $U_{nm}^\pm(\rho, z)$ are the solutions to the equations:

$$\begin{aligned} \left[-\frac{1}{2} \frac{\partial^2}{\partial \rho^2} - \frac{1}{2} \frac{\partial^2}{\partial z^2} + \frac{m^2 - 1/4}{2\rho^2} + V_{\text{eff}} - \epsilon_{nm} \right. \\ \left. \mp (\hbar\omega + i\delta) \right] U_{nm}^\pm(\rho, z) = \psi_{nm}(\rho, z) V(\rho, z). \end{aligned} \quad (11)$$

The conclusion is,

$$\begin{aligned} (\hat{\chi}_0^0 V)(\rho, z) &= \sum_{n,m} f_{nm} \psi_{nm}(\rho, z) \\ &\times [U_{nm}^+(\rho, z; \omega) + U_{nm}^-(\rho, z; \omega)]. \end{aligned} \quad (12)$$

Thus, to compute the action of $\hat{\chi}_0^0$ on an arbitrary function $V(\rho, z)$, we solve the linear equation Eq. (11) for all (n, m) indices of the occupied states and each time we update the sum in Eq. (12). Eq. (11) is solved using the same Biconjugate Gradient Algorithm as before, where the action of the reduced Kohn-Sham Hamiltonian on a function $\psi(\rho, z)$ is implemented on a grid, using a finite difference expression for the kinetic part.

The convergence of the Biconjugate Gradient Algorithm depends crucially on the initial guess. One important aspect of the present calculations is that we compute the optical spectrum for a sequence of frequencies and the computed Δn for one frequency can be used as the starting point in the Biconjugate Gradient Algorithm for the next frequency. Thus, excepting the first frequency, the iteration in the Biconjugate Gradient Algorithm converges extremely fast, typically in less than 4 steps.

The code was tested on spheres and spherical nanoshells that were considered in several of our past works. In these past works, the electronic structure and optical absorption of the systems were computed with a code that took advantage of the spherical symmetry. Using the new code that we just described above, we were able to reproduce with great accuracy both the electronic structures and optical absorption spectra for these systems.

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 2. Zangwill, A.; Soven, P. *Phys. Rev. A* **1980**, *21*, 1561–1572.
 3. Saad, Y. *Iterative Methods for Sparse Linear Systems*; SIAM: Philadelphia, USA, 2003.