Green's-function method for calculation of adsorption of organic molecules on noble metal nanoparticles

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A numerical method for the calculation of electronic structure of a nanosystem composed of a pseudoisocyanine (PIC) molecule assembled on a silver nanoparticle is developed. The electronic structure of the silver nanoparticle containing 125 atoms is calculated within the local density version of the density functional method. A model of an Ag atom embedded in the center of a spherical jellium cluster is used. The host electron Green’s function is calculated by means of the spherically symmetric expansion. The principal theoretical tool is the scattering theory using the Green’s-function method. The molecule—silver nanosystem interaction is studied using the approach similar to that of the Anderson model for transition metal impurities in solids. Localized levels are shown to split off from the top of the band of the Ag nanoparticle. The electronic structure calculations yield information on the character of chemical bonding in the PIC molecule — silver particle nanosystem.

PACS numbers:

I. INTRODUCTION

Organic-inorganic nanohybrid materials that utilize noble metals (silver or gold), functionalized with organic or biological constituents can produce unique physical and chemical properties that otherwise are not possible in single component materials. These materials have given rise to growing interest in theoretical methods that can calculate the electronic structure and transport properties of nanoscale devices. A major problem with these nanostructures is to optimally control molecular self-organization on metallic surface. J-aggregates of cyanine dyes make a fascinating topic of research due to their outstanding optical properties. Spectroscopic peculiarities are the result of exceptionally strong electronic interactions between the transition dipole moments of the dyes that give rise to extended exciton states after photo excitation. The excitonic optical spectrum depends on the details of the structural and electronic arrangement of the dye molecule.

Adsorption of dyes to nanoparticles of noble metals presents a special interest. Study of the interaction of an adsorbed dye, in both its ground and excited states, with the energy states of the conduction band of metal is also of interest and may rely on theoretical calculations of the energy electronic structure of the nanosystem made of pseudoisocyanine (PIC) assembled on a silver nanoparticle. Moreover, the nature of coupling between excitonic molecular J-aggregates and a metallic nanoparticle is still not completely understood, since to the best of our knowledge no attempts had been made to calculate the electronic structure of Ag + PIC nanosystems from the “first principles” In addition, a major problem of molecular engineering is to control molecular self-organization. This process is governed by the formation of chemical bonds, e.g. covalent or hydrogen bonds. The assembly process on nanoparticles is also affected by the molecule — substrate interactions. Therefore, understanding bonding between the molecules and nanoparticle is crucial in order to be able to choose appropriately the molecular and substrate materials for a nanosystem design. On the theoretical side, the new computational techniques allow one to predict the preferential geometry of the nanostructure arrangements as well as the strength and chemical bonds involved directly from the fundamental quantum mechanical laws.

We demonstrate how ab initio calculations allow one to explain the shape of the observed superstructures, to elucidate the role of electronic structure and the molecule — silver particle bonding and to reveal details of the nanosystems not yet experimentally accessible.

Quantum electronic-structure calculations allow us to understand the macroscopic properties of complex polyatomic systems (specifically organic PIC molecule assembled on a silver nanoparticle) in terms of the microscopic states available to the electrons described by their wave functions and the nanosystem electron density \( \rho_{\text{nano}}(\mathbf{r}) \). For these larger systems it is frequently of a greater interest to know the change in the electronic structure associated with the changes in the Kohn-Sham effective potential \( V_{\text{eff}}(\mathbf{r}) \) and the electron density. Our work develops
a theoretical technique that makes the direct calculation of such changes possible. This technique is based on the self-consistent Green’s function method and standard density-functional theory (DFT) in combination with the local-density approximation (LDA) which maps the many-electron interaction problem onto a self-consistent treatment of non-interacting quasi-particles moving in an effective potential

\[ V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + 2 \int \frac{n_{\text{nano}}(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d\mathbf{r'} + V_{\text{xc}}(\mathbf{r}), \tag{1} \]

where \( V_{\text{ext}}(\mathbf{r}) \) is the external potential and \( V_{\text{xc}}(\mathbf{r}) \) is the local exchange-correlation potential.

II. FORMULATION OF THE PROBLEM

We present in this paper results of numerical calculations of the electronic structure of nanosystem: PIC molecule + small Ag particle, whose electronic structure is described by the Hamiltonian

\[ H = H_{\text{jellium}} + H_{4d} + H_{\text{PIC}} + H_{\text{PIC-}Ag} + H_{\text{PIC-}Ag} \tag{2} \]

The first term stands for the spherical jellium cluster Hamiltonian (see below) made of 5s-valence electrons of Ag-atom. The next term in the Hamiltonian describes the subsystem of Ag 4d-electrons embedded in the spherical jellium cluster. \( H_{\text{PIC}} \) stands for the PIC molecule Hamiltonian. The last two terms of the Hamiltonian describe the resonant \( \rho(\mathbf{r}) \) (due to the presence of the 4d state of Ag atoms) and potential \( p(\mathbf{r}) \) (due to the Ag 5s states) scattering. This distinction between the two types of scattering by atomic potential is discussed in detail in Ref. [12].

The method is based on the separation of the Hamiltonian into two parts

\[ H = H_{LDA}^0 + \Delta H \tag{3} \]

Here \( H_{LDA}^0 = H_{\text{jellium}} + H_{4d} \) is the Hamiltonian of the reference system, which includes an effective single-particle LDA potential \( V_{LDA}^0(\mathbf{r}) \). \( \Delta H = H_{\text{PIC}} + H_{\text{PIC-}Ag} + H_{\text{PIC-}Ag} \) is the Hamiltonian of the "difference" system described by the potential \( \Delta \rho(\mathbf{r}) \), which is the difference between the self-consistent Kohn-Sham effective potential \( V_{\text{eff}}(\mathbf{r}) \) and \( V_{LDA}^0(\mathbf{r}) \).

Four different computation schemes are used, each of which provides mutually complementary information about the electronic spectra of complex nanosystem. The first one is the spherical jellium cluster model with the central 4d Ag atom embedded in the center of a silver nanoparticle. The second method is based on the Green’s function approach. Then the physical effect shows up exclusively in variations of the Kohn-Sham effective potential \( V_{\text{eff}}(\mathbf{r}) \) and of the nanosystem electron density \( \rho_{\text{nano}}(\mathbf{r}) \). In this approach, we follow a two-step concept and split the entire problem into two parts, where each of them is far less complicated than the original one. The whole nanosystem is decomposed into the reference system characterized by the ground-state electron density \( \rho_{LDA}^0(\mathbf{r}) \) and the difference system with the electron density

\[ \Delta \rho(\mathbf{r}) = \rho_{\text{nano}}(\mathbf{r}) - \rho_{LDA}^0(\mathbf{r}), \tag{4} \]

which is the difference between the self-consistent electron density \( \rho_{\text{nano}}(\mathbf{r}) \) of the nanosystem and the ground-state electron density \( \rho_{LDA}^0(\mathbf{r}) \) corresponding to the Hamiltonian

\[ H_{LDA}^0 = -\nabla^2 + V_{LDA}^0(\mathbf{r}) \tag{5} \]

(atomic Rydberg units are used). Here \( H_{LDA}^0 = H_{\text{jellium}} + H_{4d} \). The complete set of electronic states of the reference system is represented by the reference Green’s operator

\[ G^0(z) = (z - H_{LDA}^0)^{-1} \tag{6} \]

depending on the complex variable \( z = \varepsilon + i\eta \) (\( \eta \geq 0 \)). The calculation of \( G^0(z) \) along a properly chosen contour in the complex energy plane defines step one of our approach. As the second step, the Green’s operator \( G(z) \) of the nanocluster-assembled system (and the charge density related to it) is determined by solving the Dyson equation

\[ G(z) = G^0(z) + G^0(z) \Delta V G(z) \tag{7} \]

in a self-consistent way. A detailed description of our approach to solving Eq. (7) is presented in Appendix.

The third semiempirical method ZINDO/S was used for the calculation of electronic structure of a neutral PIC molecule. The fourth DFT/B3LYP/6-31G method was applied to the equilibrium geometry calculation of PIC molecule by the standard DFT-method.

We would like also to indicate here the limitations of our approach to the treatment of Ag + PIC nanosystem based on the spherical jellium model for the Ag nanoparticle. The previous structural research using method of the molecular dynamics shows that very diverse non-spherical geometries of the nanoparticle are possible. Relaxation of the PIC molecule and nanoparticle reconstruction in response to the PIC molecule are also not taken into account. Including all the processes into the calculation scheme can strongly complicate the procedure and we leave it for our future research.

III. CALCULATION OF THE ELECTRONIC STRUCTURE OF AG - NANO PARTICLE

First, we consider the electronic structure of silver nanoparticle. Cluster calculations are traditionally employed in studies of surface and bulk materials. They help us to understand how the physical properties evolve from a free atom to a finite-size system. In recent years,
microclusters on the basis of Ag atoms attracted a lot of interest, due to the growing technological significance of nanosystems including Ag and Au nanoparticles. A variety of theoretical models have been proposed for the calculations of cluster electronic structure. However, the most precise models allow one to obtain their electronic structure with a small number of atoms only. For large atomic aggregations, these methods cannot be applied successfully, and simpler models are employed in this case. Thus, for the study of electronic properties of sp-bonded metal clusters, a jellium model is used. But the models based on the jellium approximation are not directly suitable for the investigations of metal clusters containing atoms with localized d shells. As a consequence a model of an Ag atom embedded in the center of a spherical jellium cluster is applied for a description of a small Ag metallic nanoparticle containing localized 4d electrons. The DFT approach in the local density approximation was used in computation. The calculations have shown that the spherical jellium nanoparticle with the central Ag atom is mimicked by a single atom embedded in the center of a jellium sphere with the \( r_M \) radius, determined according to the position of the real atom with respect to the cluster surface. \( r_M \) is then the shortcut between the atom and the cluster surface.

The electronic structure of an Ag atom embedded in the jellium sphere is obtained within the DFT framework from a self-consistent solution of the Kohn-Sham equations (in atomic Rydberg units):

\[
[-\nabla^2 + V_{\text{LDA}}^0(r)]\psi_{nl}(r) = \varepsilon_{nl}\psi_{nl}(r) \tag{8}
\]

where

\[
V_{\text{LDA}}^0(r) = -\frac{2Z^0}{r} - 2\int \frac{\rho^-(r') - \rho^+(r')}{|r - r'|} dr' + V_{\text{xc}}(r) \tag{9}
\]

with the Vosko et al form \(^{22}\) of the local exchange-correlation potential \( V_{\text{xc}}(r) \). Here \( \varepsilon_{nl} \) and \( \psi_{nl} \) are single electron energies and wavefunctions, respectively; \( Z^0 \) is the nuclear charge of the Ag atom. The electron density of the jellium cluster with an Ag atom is

\[
\rho^-(r) = \sum_{nl} f_{nl} |\psi_{nl}(r)|^2 \tag{10}
\]

where the coefficients \( f_{nl} \) are the occupation numbers of the states with quantum numbers \( n, l \), and the summation is over all states of the atom-in-jellium nanoparticle. The radial distribution of the positive jellium background is given by

\[
\rho^+(r) = [3N_{\text{val}}(N_{\text{val}} - 1)/4\pi r_M^4]\Theta(r_M - r), \tag{11}
\]

where \( \Theta(x) \) is the unit step function, \( N_{\text{val}} \) is the number of atoms in the cluster (including the specific Ag atom), \( N_{\text{val}} \) is the number of valence electrons in the Ag atom. The cluster radius \( r_M \) is found from the expression

\[
r_M = N_{\text{val}}^{1/3} \rho_e, \tag{12}
\]

where \( \rho_e \) is the Wigner-Seitz radius. We have used here \( \rho_e = 3.02356 \) a.u., \( N_{\text{val}} = 125 \), and \( N_{\text{val}} = 1 \). The numerical integration of the Kohn-Sham equation for the Ag atom in a jellium sphere is carried out by means of the Milne method.\(^{22}\) The free Ag atom eigen-energies \( \varepsilon_{nl} \) and wave-functions \( \psi_{nl} \) are calculated by means of the semirelativistic RATOM program.\(^{22}\) The self-consistency procedure for the potential \( V_{\text{LDA}}^0(r) \) is carried out in a mixed fashion. The first two iterations use the arithmetic average scheme, which later on is effectively substituted by the Aitken scheme.\(^{22}\)

The electronic ground-state configurations of the jellium sphere containing the central Ag atom were determined in the following way. The rules for the energy level occupation separately in jellium and in a free atom are well known. Clearly, insertion of an atom into the jellium sphere center does not change the atom and jellium field symmetry, and, consequently, the symmetry of their electronic states is not changed either. One can suppose therefore that the number of electron states with the same symmetry in the jellium sphere with the central atom is equal to the sum of such symmetry states of the jellium and the atom. The sequence of energy levels of atom-in-jellium is obtained by solving the self-consistent equations [8] - [10] for the different angular \( l \) and principal \( n \) quantum numbers. The energy levels are occupied in accordance with the Pauli principle. The highest levels can be partially occupied.

We have computed the total energy of the jellium spheres with the Ag atom in the center for various occupation numbers of the upper levels. For the calculation of the total energy we employed the equation

\[
E_{\text{tot}} = \sum_j \varepsilon_j + \int \rho_{\text{out}}(r) \times \left[ \varepsilon_{\text{xc}}^\text{out}(r) - V_{\text{xc}}^\text{in}(r) + \int \frac{\rho_{\text{out}}(r') - 2\rho_{\text{in}}(r')}{|r - r'|} dr' \right] dr. \tag{13}
\]

Here the indices in and out indicate the input and output data of the latest self-consistency iteration, respectively; \( \varepsilon_{\text{xc}}^\text{out}(r) \) is the exchange correlation energy density of a homogeneous electron gas with the density \( \rho_{\text{out}}(r) \) parameterized according to Vosko et al.\(^{22}\)

The calculations have shown that the spherical jellium nanoparticle with the central 4d Ag atom has the following energy spectrum. The eight lowest energy levels are identical to those of the 4d atom core; the rest of them are similar to the states in a spherical potential well. In this paper the quantity \( n = n_n + 1 \) has been considered as the principal quantum number; \( n_n \) is the number of nodes of the wave-function of the corresponding energy level. Thus, the electronic configuration of the central Ag atom in the jellium sphere is \( 1s^22s^22p^63s^22p^61d^{10}4s^23p^6 \). The electronic states of the 125 atoms are arranged in the following order: \( 2d^{10}1f^{14}g^{18}1h^{22}2f^{14}11^{26}1j^{30} \). The self-consistent potential \( V_{\text{LDA}}^0(r) \) (Eq. [9]) with the elec-
FIG. 1: (Color online) A self-consistent Ag-nanoparticle potential of the jellium sphere containing the central Ag atom (the radial distribution, in atomic units). The states of subshell 2d^{10} are split into 4f^{5/2} and 4d^{3/2} levels due to the spin-orbit interaction.

tronic levels for an Ag atom embedded in a jellium sphere is presented in Fig. 1.

An important characteristic of the Ag nanoparticles is their ionization potential (IP). It has been shown in Ref. 27 that a strong correlation exists between the chemisorption reactivity of a small transition metal cluster and its ionization threshold. Here we report the IP’s for the Ag nanoparticles containing up to 160 atoms. In these calculations we simulate atoms of an Ag nanoparticle by Ag atoms embedded in the center of jellium spheres of various sizes. The jellium sphere radius \( r_M \) is defined by the short cut between the atom and the cluster surface.

The IP of an atom-in-jellium was obtained using the ground state theory (LDA-method) by self-consistent calculation according to Eq. (13) and subtraction of the total energies of neutral and ionic ground states. It was found that the ionization thresholds of atoms of the Ag nanoparticles differ and depend on the position of the atoms with respect to the cluster surface. The lowest atomic ionization threshold has been chosen as the IP of the Ag nanoparticle. For the neutral Ag atom we obtained \( IP_{atom}^{theor} = 7.96 \text{ eV} \) and \( IP_{atom}^{exp} = 7.57 \text{ eV} \). Instead of calculating the IP’s from the data as the total energy differences between the neutral cluster and ions, we use an alternative method, based on the Slater transition state approach and Janak theorem for the density functional theory, which allow us to calculate the excitation energy of adding (removing) an electron to (from) the system from (to) the infinity. This scheme can be derived in the following way. The total energy \( E_{tot} \) difference between the final and initial states for the process of electron addition to the one-electron state \( j \) can be calculated as an integral of total energy derivative with respect to the occupancy \( q_j \). This derivative,

\[
\varepsilon_j = \frac{\partial E}{\partial q_j},
\]

corresponds to the Kohn-Sham eigenvalue

\[
E(q_j = 1) - E(q_j = 0) = \int_0^1 dq_j \varepsilon_j(q_j) \simeq \varepsilon_j(0.5). \quad (14)
\]

Eq. (14) becomes exact if the LDA eigenvalue \( \varepsilon_j(q_j) \) is a linear function of the occupancy, which is usually true to within a good accuracy.

The vertical (or adiabatic) ionization potentials of the clusters are evaluated from the highest occupied molecular orbital (HOMO) energy of the neutral clusters. The calculated IP of an \( \text{Ag}_{125} \) nanoparticle is \( IP_{theor} = 4.73 \text{ eV} \). When the number of atoms in the nanoparticle increases the IP converges to the work function \( \Phi \) of the corresponding metallic half-space. The work function of 4.46 eV was determined experimentally for \( \text{Ag}(111) \). Our calculation yields the value of 4.73 eV for \( IP_{theor} \). The LDA HOMO-LUMO (lowest unoccupied molecular orbital) gap between occupied \((\varepsilon_{2p})\) and unoccupied \((\varepsilon_{g\gamma})\) orbitals for the Ag nanoparticle is \( \Delta^{\text{HOMO}–\text{LUMO}} = \varepsilon_{12p} - \varepsilon_{2g\gamma} = 1.58 \text{eV} \).

It is well-known that Ag aggregates are formed in a colloidal aqueous solution of NaCl. Therefore studying electronic properties of small metallic particles in different dielectric matrices presents a great scientific and practical interest as well as those of free Ag nanoparticles. When a metallic particle is placed in a dielectric medium, polarization changes \( \rho_{pol}(r) \) are induced on the particle surface, which produce the potential

\[
V_{pol}(r) = 2 \int \frac{\rho_{pol}(r'')}{|r - r'|} \; dr'' \quad (15)
\]

In Ref. 33 we have shown that the ground state of a metal nanoparticle embedded in a dielectric matrix can be described by the self-consistent Kohn-Sham equations with the effective potential

\[
V^\varepsilon(r) = V(r) + V_{pol}(r) \quad (16)
\]

where \( V(r) \) has the same form as the effective potential for the nanoparticle in vacuum. Averaging \( V_{pol}(r) \) and substituting the result into (16) yields

\[
V^\varepsilon(r) = \begin{cases} 
V(r) + \frac{1-\varepsilon}{\varepsilon} V(M) & r \leq r_M, \\
V(r)/\varepsilon & r \geq r_M.
\end{cases}
\]

The calculations for the \( \text{Ag}_{125} \) nanoparticle embedded in a dielectric medium with the relative permeability \( \varepsilon = 61.1 \) (50% water solution of NaCl) have shown that with the increasing dielectric permeability \( \varepsilon \) the potential profile near the jellium edge becomes steeper. The bottom of the potential well \( V_{bottom} \) and the single electron energy levels \( \varepsilon_j \) rise when the cluster is embedded in a dielectric matrix. It should be emphasized that the oscillations in the electronic density of jellium cluster in vacuum are suppressed in the dielectric media. The
amount of the electronic charge beyond the jellium edge (electronic "spill out") increases with the increasing $e$. This is caused by a positive shift of the electronic eigenenergies of Ag nanoparticles in a dielectric medium and an extension of the corresponding wave functions.

The static dipole polarizability is also well-known to be intimately related to the electronic structure of a nanocluster. We discuss here the photo-response of an isolated Ag nanoparticle to an external electromagnetic field in terms of the frequency-dependent polarizability.

$$\alpha(\omega) = -\frac{8\pi}{3} \int_0^\infty dr' r'^3 \delta \rho(r', \omega)$$  \hspace{1cm} (17)

where $\delta \rho(r', \omega)$ is the change in the charge density. The calculation of the static dipole polarizability $\alpha(\omega = 0)$ for an Ag nanoparticle is carried out within the time-dependent local-density approximation (TDLDA) using the self-consistent solution of the set of equations

$$\delta \rho(r, \omega) = \int \chi_0(r,r'; \omega) \delta V(r') dr',$$  \hspace{1cm} (18)

$$\delta V(r, \omega) = V_{ext}(r, \omega) + V_{ind}(r, \omega),$$  \hspace{1cm} (19)

and

$$V_{ind}(r, \omega) = 2 \int_0^\infty \frac{\delta \rho(r', \omega)}{|r-r'|} dr' + \frac{\partial V_{xc}(r)}{\partial \rho(r)} \delta \rho(r, \omega).$$  \hspace{1cm} (20)

Here $V_{ext}(r, \omega)$ and $V_{ind}(r, \omega)$ are the external field with the frequency $\omega$ and the induced field, respectively; $\chi_0(r,r'; \omega)$ is the susceptibility function in the independent-particle approximation. For $r_M = 15.1178$ a.u. (Ag$_{125}$ cluster) $\alpha(\omega = 0) = 4.82 \text{Å}^3$/atom. The bulk atomic polarizability is $4.33 \text{Å}^3$/atom.

IV. RESULTS AND DISCUSSION

We present here a theoretical approach to the organic molecules interacting with silver in terms of numerically solvable DFT-models. In practice, these models apply to nanosystems (PIC-molecule on Ag-particle) and provide an understanding of doping silver nanoparticles by PIC adsorbates. The chemical structure of PIC molecule is exhibited in Fig. 2. The density-functional calculations are performed in order to determine the equilibrium structure of these PIC molecules by the DFT/B3LYP/6-31G-method. The molecule geometries are optimized using the B3LYP-exchange-correlation energy functional and potential. The minimum basis set is capable of producing reasonable results is 6-31G. Since the geometry of PIC within the Ag+PIC-nanosystem is undoubtedly disturbed as compared to the PIC monomer and possibly resembles a PIC aggregate, these calculations were performed as follows. First, the equilibrium geometry of the tetramer (PIC:Cl)$_4$ was found. After that, the averaged geometry of the monomer (PIC:Cl) was obtained by averaging over four molecules of the tetramer. The search of the equilibrium geometry of tetramer was performed by standard density functional method DFT/B3LYP/6-31G using GAMESS program package. The electronic structure of a neutral PIC molecule was calculated by ZINDO/S-method.

It is assumed that the PIC molecule is adsorbed on the spherical surface of an Ag nanoparticle, setting down over the sphere so that its central carbon atom (the molecule center of gravity) is positioned in the point $(2.223, 0.680, 0.705)$ Å with respect to the center of Ag nanoparticle. In the beginning we present the results of calculation of the electronic structure of an Ag$_{125}$ nanoparticle obtained by the model of an atom in the center of a spherical jellium sphere and DFT in the local density approximation. Fig. 3 presents the energy level structure of the Ag jellium nanoparticle with 134 valence electrons (the Ag atom core electrons orbitals lie below $\varepsilon_{3p^{1/2}} = -4.27$ Ry).

Fig. 4 shows the Ag bound states by the red line. The peak heights are proportional to the degeneracy. The continuum density of states $\Delta n(\varepsilon)$ is given for the positive energies corresponding to the delocalized (unoccupied) states by Eq. (A18). Fig. 5 exhibits the contribution of potential scattering [Eq. (A17)] to the formation of Ag related bound states ($\varepsilon_{2g} = -1.34$ eV) and fall in the broad range $\Delta^{\text{HOMO-LUMO}}$. This level is obtained from Eq. (A17) with $\tilde{M}$ substituted for $Q^{-1}$ [see Eq. (A11)]. The states $2d^{10}(4d^{5/2} + 4d^{3/2})f^{14}g^{18}h^{22}l^{14}i^{26}j^{30}$ in the occupied part of the spectrum are the Ag reso-
nances in the band (red line in Fig. 3) and lie in the interval (-10,-5) eV. The resonant $\varepsilon_{2g}$ level [see Fig 3] arises at the energy 0.24 eV below the LUMO-level. Both the Ag resonances and $\varepsilon_{2g}$ states are found in the solution of Eq. (A17) with the full self-energy $\hat{M}(z)$.

The calculation of $\text{Ag}_{125}$ particle embedded in a dielectric medium with relative dielectric permeability $\varepsilon = 61.1$ (50% water solution of NaCl) have shown that the electronic "spill out" increases in the dielectric medium as compared to vacuum and is equal for this case to 21.6 electrons.

The 26.14 eV width band of Ag+PIC nanostructure is formed by strongly hybridized C(s,p) (blue line), N(s,p) (yellow line), H(s) (black line) and Ag (red line) states. The unoccupied states lie above $\varepsilon_{\text{LUMO}} = -1.58$ eV. Furthermore, we find the acceptor-like $\varepsilon_{2g}$ states almost entirely localized in the adsorbate PIC molecule and hybridized with the hydrogen 1s levels. As discussed in Ref. 45, the interaction between the adsorbate and the transition metal surface can be described as a two-state problem (adsorbate state and the d-band) leading to formation of bonding and anti-bonding states. Thus, an upshift of the d-states should increase the adsorbate-metal interaction, since it would lead to the formation of an anti-bonding orbital closer to the Fermi level. Strong features appearing between -5 and -10 eV represent formation of a bonding orbital through the interaction of hydrogen 1s state with the metal d-band, and this formation is typical for all transition metals. The bonding Ag 2d-1s states lie around -9 eV. The anti-bonding orbital lies around $\varepsilon_{\text{LUMO}}$ level and is hybridized with the resonance $\varepsilon_{2g}$ states.

We will interpret the density of states (see figure 3) of nanosystem Ag+PIC species basing on their bonding properties obtained from the Green’s function calculations and simple molecular orbital considerations.

For a more detailed study of the chemical bonding in these nanosystem we have calculated the electron-density change $\Delta\rho(r)$ (see figure 4).

The electronic structure obtained for the Ag+PIC nanosystem has a terminal Ag—C bond. Similarly to all transition metals the C—C bond is known to be much stronger than the Ag—C bond. Thus, it is not energetically favorable for Ag to enter the C chain, since this will break the stronger C—C bonds and form weaker Ag—C bonds. The Green’s function calculations indicate that the excited Ag atoms in the nanosystem are involved in the chemical bonding. Simple molecular orbital considerations suggest that the C atom directly bonded to an Ag atom must be in an sp-hybridized state in order to more effectively interact with the Ag particle orbitals. And the Ag 2d orbitals can interact with the other p orbitals of the C atoms to form additional bonds. Thus, our calculations show that the Ag(d,s) — C(s,p) bond is of a considerable importance for understanding the nature of chemical bonding of Ag+PIC nanosystem.

As shown in Fig. 4, all Ag states are situated between the C-states. From $\Delta n(\varepsilon)$ distribution as well as from its partial components $\Delta n_s(\varepsilon)$, $\Delta n_p(\varepsilon)$ and $\Delta n_d(\varepsilon)$, one can conclude, that $d - s, p$ resonance is observed in (Ag+PIC)-nanosystem, was revealed in the compounds of metals, containing the filled d-shells, with non-metals. In this case the Ag 5s-type states $(1f^{14}1g^{18}1h^{22}2f^{14}1i^{26}1j^{30})$ form $\sigma$ bonding and $\sigma^*$ anti-bonding orbitals with the C sp- hybridized orbitals. At the same time, the 2d$\pi$ orbitals in Ag can interact with the C—C $\pi$ orbitals. The resonance of the HOMO $\varepsilon_{2g}$ with the hydrogen 1s-level ($\sigma^*$-symmetry) is the principle interaction in the Ag$5\sigma$—H1s bond. This bond plays the crucial part in determining the chemisorption reactivity.

There are two factors that affect this orbital interac-
tion, first the HOMO energy, and second and more importantly, the symmetry of the HOMO. It follows from Ref. 48 that the d-symmetry HOMO would have lead to a high reactivity. However, the $\varepsilon_{2g}$ HOMO is mainly of $5s$ character and is not symmetry matched with the H $\sigma^*$ orbital, hence it results in an extremely low reactivity. Thus, the s-type HOMO of the $Ag$+PIC nanosystem effectively provides a shielding effect to protect the nanosystem from being attacked by the hydrogen atoms.

Fig. 3 shows the charge density difference of an $Ag$+PIC nanosystem

\[ \Delta \rho(r) = \rho^{Ag+PIC}(r) - \rho^{Ag}(r) - \sum_a \rho^{atom}_a. \]

Here, $\rho^{Ag+PIC}(r)$ is the self-consistent electron density of the $Ag$+PIC nanosystem; $\rho^{atom}_a$ is the electron density of the free atoms in the PIC-molecule; $\rho^{Ag}(r)$ is the density in reference system. The $Ag$ sphere with radius 15.12 a.u. is also schematically shown. The electronic-density change is close to $z = 1.33$ a.u. Fig. 3 reveals that the electron density change $\Delta \rho(r)$ is strongly localized. We see also that the adsorbed PIC-molecule causes an accumulation of the reference charge on $Ag$-metal side due to the three carbon atoms with the coordinates (14.21, -13.71,1.33) a.u., (12.13,-12.03,0.99) a.u., (13.93,-16.37,1.31) a.u. and one hydrogen atom with the co-ordinates (15.25,-17.37,2.26) a.u. Based on the chemical bonding model of the carbon and hydrogen valences, the chemical structure of interaction between the $Ag$ and (C,H) atoms of PIC-molecule has the form

\[ H - Ag - C = C - C - H \]

The major part of electron density in $C = C$ and $C = N$ bonds is localized at the bottom of the band and have the $sp$ and $sp^2$ type covalence of the chemical bonding. At the same time, the upper part of the occupied states contain mainly the bonding electrons which are concentrated in $Ag-H$ and $Ag-C$ bonds and have $(d, s)$-$(s, p)$ resonance type of bonding with the maximum displacement towards the $Ag$ nanoparticle.

**V. CONCLUDING REMARKS**

Carrying out a numerical solution of the Dyson equation [47] in the Kohn-Sham density-functional methodology we determined the electronic and chemical structure of $Ag$+PIC nanosystems. The calculation of $Ag_{125}$-particle embedded in a dielectric medium with the relative permeability $\varepsilon = 61.1$ (50% water solution of NaCl) shows that the amount of the electronic charge beyond the jellium edge (electronic "spill out") increases in the dielectric medium as compared to the vacuum and equals in this case 21.6 electrons. The resonant $\varepsilon_{2g}$-level [see Fig. 3] arises at the energy 0.24 eV under the LUMO-level. Both the $Ag$ - resonances and $\varepsilon_{2g}$ states are found as solutions of Eq. (A1) with the full self-energy $\tilde{\Sigma}(z)$. The electronic structure obtained for the $Ag$+PIC nanosystem has a terminal $Ag-C$ bond.

Three $C$ atoms and one $H$ atom take part in the adsorption of the PIC molecule on the $Ag$ nanoparticle and accumulation $\Delta \rho$ of charge takes place. The hybridized $Ag-H$ and $Ag-C$ bonds are of the $(d, s)$-$(s, p)$ resonance type with the maximal displacement of charge towards the $Ag$ nanoparticle.

**Acknowledgment** Authors are indebted to K.Kikoin for detailed discussions. This work was supported by the Russia-Israel Scientific Research Cooperation, grant N 3-5802 (B.F. and V.M.) and the Israel-US Binational Science Foundation (B.F.), grant N 2008282.

**Appendix A: Green’s-function technique to calculate the electronic properties of organic admolecule on metal cluster**

Our approach is based on the general concept formulated in Ref. 47. It makes it possible to calculate the electronic structure of metallic substrates and to study the behavior of a compact cluster adsorbed on a nanoparticle. The principal theoretical tool is the scattering theory formalism, which considers perturbation of a metal substrate single electron potential by a spatially compact cluster, which is itself compact by virtue of screening. It can therefore be treated as a localized scattering potential for $Ag$ electrons of the substrate. In order to obtain the electronic structure of admolecule on an $Ag$ nanoparticle a "matrix" scattering approach is adopted. Our objective is to construct the Green’s function matrix $G_{\mu\nu}(z)$ for the perturbed system, e.g., silver nanoparticle with organic PIC-molecule.

The theoretical analysis providing us with a link between the nanosystem and the related simple systems (Ag nanoparticle and PIC-molecule) is based on the Dyson equation [47]. As is well known, the original problem of solving a linear differential equation can be mapped onto the solution of a matrix equation of infinite dimension by expanding the wave functions in terms of a linear combination of properly chosen orthonormal functions, e.g. atomic orbitals (LCAO’s) that are used here. In most cases of the LCAO cluster calculations Slater-type orbitals strongly facilitate the numerical calculation of overlap integrals.

In practical calculations we construct the Green’s function matrix $G_{\mu\nu}(z)$ using a finite set of $N_\alpha$ basis functions $\chi_\alpha(r)$. The basis set only needs to cover the real space, within which $\Delta \rho(r)$ is localized. We will denote this region as box $A$ of volume $\Omega_A$. In the present implementation of our method the $\chi_{n\ell m}(r)$ are the Kohn-Sham orbitals

\[ \chi_{n\ell m}(r) = \psi_{n\ell m}(r - R_\alpha) | Y_{|r - R_\alpha|, \phi_{r - R_\alpha}} \]  

placed at appropriately chosen positions $R_\alpha$ in the PIC assembled molecule. Here we choose the basis of atomic functions so that $\mu = n\ell m$. $\psi_{n\ell m}(r)$ are the Kohn-Sham
radial wave functions obtained with the help of the potential \(\Delta V(r)\), which in turn is calculated by means of the functions \(\psi_{nlm}(r)\). The selfconsistency iterations are repeated until a desired convergence is achieved. \(Y_{lm}(\theta, \phi)\) are the spherical harmonics centered at \(R_\alpha\).

Writing the Dyson equation
\[
G(z) = G^0(z) + \Delta G(z) \tag{A2}
\]
we see that only the difference operator \(\Delta G(z)\) (and the difference electron charge density \(\Delta \rho(r)\) related to it) need to be actually calculated. This difference operator has the form
\[
\Delta G(z) = \left[ (1 - \tilde{G}^0(z) \cdot \Delta V \cdot (L^{-1})^\dagger)^{-1} - 1 \right] \tilde{G}^0(z)
\]
where
\[
\Delta V_{\mu\nu} = \int_{\Omega_A} \chi^*_\mu(r) \Delta V[r(r)] \chi_\nu(r) dr
\]
and \(I\) is a unit matrix. Here the factor \(L^{-1}\) ensues from the assumption that the basis set \(\chi_\mu(r)\) was used in the Cholesky decomposition \(S = L \cdot L^\dagger\) for the overlap matrix
\[
S_{\mu\nu} = \int_{\Omega_A} \chi^*_\mu(r) \chi_\nu(r) dr
\]
in order to obtain the orthonormal basis.

The density variation is calculated using the equation
\[
\Delta \rho(r) = \text{Im} \sum_{\mu=1}^{N_h} \sum_{\nu=1}^{N_b} \tilde{\Delta} \rho_{\mu\nu} \chi_\mu(r) \chi^*_\nu(r) \tag{A3}
\]
where
\[
G^0_{\mu\nu}(z) = \left( (L^{-1})^\dagger G^0(z)L^{-1} \right)_{\mu\nu},
\]
\[
\tilde{\Delta} \rho_{\mu\nu} = \left( (L^{-1})^\dagger \Delta \rho L^{-1} \right)_{\mu\nu}
\]
and
\[
\Delta \rho = -\frac{1}{\pi} \int_{\varepsilon_h}^{\varepsilon_{\text{HOMO}}} \Delta G(z) dz. \tag{A4}
\]
The lower integration limit \(\varepsilon_h\) is chosen in such a way as to include all the relevant Ag and molecule states, \(\varepsilon_{\text{HOMO}}\) is the HOMO energy. To compute the integral \([A3]\), we introduce a contour \(C\) in the complex plane \(z\) enclosing all the poles of the Green’s function up to the highest occupied molecular orbitals energy in the charge density calculation.

Our computational scheme is based on the spherically symmetric Ag metallic nanoparticle Green’s function
\[
G^0(r, r'; \varepsilon) = \sum_{lm} Y_{lm}(\theta, \phi) G^0_l(r, r'; \varepsilon) Y^*_{lm}(\theta', \phi'), \tag{A5}
\]
decomposed in terms of the spherical harmonics. Here
\[
G^0_l(r, r'; \varepsilon) = \frac{R_l(r_<, \varepsilon)N_l(r_>, \varepsilon)}{r^2 W_l(\varepsilon)}, \tag{A6}
\]
with \(r_< = \min(r, r')\), \(r_> = \max(r, r')\). \(R_l(r_<, \varepsilon)\) and \(N_l(r_>, \varepsilon)\) are the regular and nonregular solutions of the radial Kohn-Sham equations with the potential \(V^0(r)\) and energy \(\varepsilon\). \(W_l(\varepsilon)\) is the Wronskian of the functions \(R_l\) and \(N_l\). We obtain \(R_l\) and \(N_l\) by integrating the radial Kohn-Sham equation, using the asymptotic behavior of these functions at the origin and infinity. As is generally known, the regular solution \(R_l\) behaves asymptotically as \(r^{l+1}\) at \(r \to 0\). When \(r \to \infty\), the nonregular solution \(N_l\) must be an outgoing wave for the continuum-energy region \((\varepsilon > 0)\), and it exponentially decreases for the bound-state region \((\varepsilon < 0)\).

The Green’s function of the nanoparticle is projected onto the localized basis
\[
G^0_{\mu\nu}(\varepsilon) = \sum_{lm} \langle \mu|\Theta_A|R_l(r_<, \varepsilon) \rangle \langle N_l(r_>, \varepsilon)|\nu\rangle / W_l(\varepsilon). \tag{A7}
\]
The following notations has been used above:
\[
\langle \mu|\Theta_A|R_l(r_<, \varepsilon) \rangle = \int_{\Omega_A} \chi^*_\mu(r-R_\alpha) R_l(r_<, \varepsilon) dr,
\]
\[
\langle \mu|\Theta_A|N_l(r_>, \varepsilon) \rangle = \langle \mu|\Theta_A|N_l(r_>, \varepsilon) \rangle^*,
\]
\[
\langle \nu|\Theta_A|N_l(r_>, \varepsilon) \rangle = \int_{\Omega_A} \chi^*_\nu(r-R_\beta) N_l(r_>, \varepsilon) dr,
\]
\[
\Theta_A(r) = \left\{ \begin{array}{ll}
1, & \text{r} \in \Omega_A - \text{volume of the box region A} \\
0, & \text{otherwise,}
\end{array} \right.
\]
Here we use the single-center method to compute all integrals in the Slater-type orbital basis. The Slater orbital centered in a point, defined by its location vector \(R_\alpha\), is usually
\[
\chi_{nlm}(r) = N_{nl} |r - R_\alpha|^{|n-l-1|} \exp(-|\zeta| |r - R_\alpha|) \times Y_{lm}(\theta_{r-R_\alpha}, \phi_{r-R_\alpha}) \tag{A8}
\]
The radial part of the Slater orbital is expanded over the Barnett- Coulson/Löwdin function (BCLF).
\[
| r - R_\alpha |^{-|n-l-1|} \exp(-|\zeta| |r - R_\alpha|) = \frac{1}{\sqrt{R_\alpha^l}} \sum_{\lambda} (2\lambda + 1) A_{\lambda+1/2}^{-l}(\zeta, R_\alpha, r) P_{\lambda}(\frac{R_\alpha \cdot r}{R_\alpha r}) \tag{A9}
\]
where $P_n(z)$ are the Legendre polynomials of degree $n$ and $A_{\lambda+1/2}^{\nu}\!(\zeta, R_\alpha, r)$ are the BCLF’s defined by the recursion

$$A_{\lambda+1/2}^{\nu}\!(\zeta, R_\alpha, r) = -\frac{\partial}{\partial \zeta} A_{\lambda+1/2}^{\nu}\!(\zeta, R_\alpha, r)$$

with

$$A_{\lambda+1/2}^{0}\!(\zeta, R_\alpha, r) = I_{\lambda+1/2}(\zeta \rho_{<}) K_{\lambda+1/2}(\zeta \rho_{>})$$

where $I_{\lambda+1/2}(z)$ and $K_{\lambda+1/2}(z)$ are the modified Bessel functions of the first and second kind; the variables $\rho_{<}$ and $\rho_{>}$ stand for the $\min(R_\alpha, r)$ and $\max(R_\alpha, r)$ respectively. In the present implementation of our method the Kohn-Sham orbitals are placed at appropriately chosen positions $R_\alpha$.

Information on the Ag+PIC adsorption can be produced from the Dyson equation that describes the interaction between the free molecule and silver particle. In this Dyson equation the part of the unperturbed Green’s function is played by the Augmented Green Function

$$G_{\text{Ag}+\text{PIC}}^{\text{NS}}(z) = \begin{pmatrix} G_{\text{PIC}}^{0}(z) & 0 \\ 0 & G_{\text{Ag}}^{0}(z) \end{pmatrix} \quad (A10)$$

In order to describe the molecule — silver nanoparticle interaction we use the approach known in the theory of transition metal impurities in semiconductors. The terms in the model Hamiltonian for Ag+PIC nanosystem are written as

$$H_{\text{PIC} - \text{Ag}} = \sum_{k i a} M_{k i a} c_{k}^\dagger d_{i a}^\alpha + h.c.$$ 

and

$$H_{\text{PIC} - \text{Ag}}^{p} = \sum_{k k' c k c'} W_{k k'} c_{k}^\dagger c_{k'}$$

Here, $c_{k}$ ($d_{i a}^\alpha$) and $c_{k}^\dagger$ ($d_{i a}^\alpha$) denote the usual fermionic annihilation and creation operators, respectively, which are labeled by the indexes, $k$ and $i_{a}$, containing site, orbital and spin degrees of freedom; $M_{k i a}$ is the $s, d$-$i_{a}$ hybridization matrix element, and $W_{k k'}$ is the matrix element for the Ag particle short-range potential scattering (the subscript “$a$” refers to the $a$-th adatom in the PIC-admolecule and $i_{a}$ stands for the corresponding electronic state and atom site). The Dyson equation reads

$$G_{i_{a} i_{a}}(z) = G_{i_{a} i_{a}}^{\text{NS}}(z) [1 + \tilde{M}_{i_{a}}(z) G_{i_{a} i_{a}}(z)] \quad (A11)$$

where

$$G_{i_{a} i_{a}}^{\text{NS}}(z) = \frac{1}{z - \varepsilon_{i_{a}} - \Delta V_{i_{a} i_{a}}}$$

Off-diagonal elements even for the nearest neighbors are up to two orders of magnitude smaller than the diagonal ones, and are neglected.

The PIC electron levels $\varepsilon_{i_{a}}$ are found self-consistently as solutions of the Kohn-Sham equations for the PIC-related orbitals in the nanosystem environment. The self-energy $\mathcal{M}_{i_{a}}(z)$ contains two contributions. The term

$$\mathcal{M}_{i_{a}}(z) = \sum_{k} |M_{k i_{a}}|^{2} \left( \frac{1}{z - \varepsilon_{k}} \right) \quad (A12)$$

describes the hybridization between the $s, d$-PIC-orbitals ($\psi_{k}$) and the Ag electrons ($\psi_{k}$) with the matrix element

$$M_{k i_{a}} = \int_{\Omega_{A}} \psi_{k}(r) \Delta V(r) \psi_{i_{a}}(r - R_{\alpha}) dr. \quad (A13)$$

The factor

$$Q(z) = 1 - \Delta V_{\text{pot}} G_{\text{Ag}}^{0}(z). \quad (A14)$$

de in Eq. (A11) describes the short-range potential scattering, where

$$\Delta V_{\text{pot}} = \sum_{k k' c k c'} \int \psi_{k}(r) \Delta V(r) \psi_{k'}(r) dr. \quad (A15)$$

and

$$G_{\text{Ag}}^{0}(z) = \sum_{k} \langle k | (z - H_{\text{LDA}}^{0})^{-1} | k \rangle = \sum_{k} \frac{1}{z - \varepsilon_{k}} \quad (A16)$$

is the single-site lattice Green’s function for the electrons in the Ag host cluster described by the Hamiltonian $H_{\text{LDA}}^{0}$.

The Ag electron levels $\varepsilon_{k}$ are found self-consistently as solutions of the Kohn-Sham equations for Ag-related orbitals in the nanosystem environment. The Green’s function describes the hybridization between the PIC-electron orbitals and the electrons in the silver host cluster, where the Ag electrons are influenced by the potential scattering due to $\Delta V$. If this scattering is strong enough, it results in splitting off of localized levels from the top of the band. This effect is also taken into account in Eq. (A11): the positions of the corresponding localized levels before the hybridization are determined by the zeros of the function $Q(z)$ in the energy gap $\Delta_{\text{HOMO-LUMO}}^{\text{LDA}}$ of the Ag+PIC nanosystem, which arises in the electronic structure due to the potential scattering only. As a result the equation for the deep level energy determined as a pole of the Green’s function [Eq. (A11)] within the framework of the LDA technique reads

$$z - \varepsilon_{i_{a}} - \Delta V_{i_{a} i_{a}}^{\text{LDA}} = \tilde{M}_{i_{a}}(z) \quad (A17)$$

It takes into account the resonance part of the scattering amplitude in the $i_{a}$ (PIC) channel and its mixing with the potential scattering states arising in the $k$ (Ag) channel.
The imaginary part of the Green’s function yields the spatial and energy electron distribution

\[ \rho(\mathbf{r}, \varepsilon) = \frac{-2}{\pi} \text{Im} G(\mathbf{r}, \mathbf{r}; \varepsilon). \]

Integrating over the energy we get the charge density distribution, whereas the local density of states, e.g., in the cell \( \Omega_A \), reads

\[ n_{loc}(\varepsilon) = \int_{\Omega_A} \rho(\mathbf{r}, \varepsilon) d\mathbf{r} \]

The change of the density of states is

\[ \Delta n(\varepsilon) = \text{Tr}(G_{Ag} + P_{IC}) - \text{Tr}(C^0_{Ag}) \]

or after straightforward calculations

\[ \Delta n(\varepsilon) = \frac{2}{\pi} \text{Im} \sum_{i_n} \frac{d}{d\varepsilon} \ln[(z - \varepsilon_{i_n} - \Delta V_{i_n i_n}) Q(\varepsilon) - \mathcal{M}_{i_n}(z)] \quad (A18) \]

The problem is treated self-consistently, starting with the trial set of LCAO Slater-type functions. The difference potential in the zero approximation is a sum of the atomic potentials of the nanosystem. The self-consistency procedure for \( \Delta V(\mathbf{r}) \) is carried out in a mixed fashion. The first two iterations use the arithmetic average scheme, which later on is effectively substituted by the Aitken scheme. Just seven iterations produce a \( 10^{-4} \) Ry selfconsistency.

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