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First principles study of the electron density distribution in a pair of bare metallic electrodes

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Abstract Self-consistent calculations of electron density distribution from first principles for a series of semi-infinite metals show that the electron density almost drops to zero at 8.5 a.u. away from a metal surface. The electron densities in a series of bimetallic-electrode systems with a distance between the two electrodes of 21.7 a.u. are further investigated. Spin-polarized calculations of electron density for nonmagnetic and magnetic bimetallic-electrode systems are compared. Our work is helpful for first principles investigation of spin-dependent metal–molecule–metal tunneling junctions.

1 Introduction

The theories of metal surface lag far behind bulk properties theories of metals due to the great additional difficulties produced by the rapid decrease of electron density near the metal surface and the loss of translational symmetry [1]. A fully self-consistent calculation of electron density distribution near a metal surface has been obtained by Lang et al. [1]. In that calculation, the jellium model was used with the positive charges being replaced by a uniform charge density background. Two planar metallic electrodes with a single atom in the region between them were further modeled to simulate an atom being transferred between tip and sample in the scanning tunneling microscope (STM) [1]. Recently, many studies based on nonequilibrium Green's function combined with density functional theory have been performed for the molecule-transport system [2, 3]. Due to the simplicity and practicability of the jellium model, some first principles studies based on the jellium model are also performed to investigate the electronic transport properties of metal–molecule–metal tunnel junctions [4–7]. Nevertheless, a spin-polarized electron density calculation using jellium model for the molecular junction has not been performed up to now. On the other hand, magnetic electrodes and/or spin-dependent metal–molecule–metal tunnel junctions have been studied intensively in the experimental works [8–13], which calls for a spin-polarized theoretical study of metal–molecule–metal tunnel junctions. The present work develops the program based on jellium model [4–7] to perform spin-polarized electron density calculations of a magnetic metal surface and of a magnetic bimetallic-electrode system, which makes an important step toward the spin-polarization study of the metal–molecule–metal tunnel junctions.

2 Computational details

A semi-infinite metal model is taken to study the metal surface problem. The jellium model is used and the uniform positive charge density $\overline{n}$ is represented by r_s (where $\overline{n} = 3/(4\pi r_s^3)$). The origin of the coordinate is set at the metal surface and the different distance away from the metal surface is denoted by coordinate x, which is along the surface normal. Therefore the positive charge density is $\overline{n}$ for $x \leq 0$ and zero for $x > 0$. Two planar metallic electrodes with a distance of 21.70 a.u. are constructed as a bimetallic-electrode system. The origin of the coordinate of the system is set at the metal surface of the left electrode. The positive

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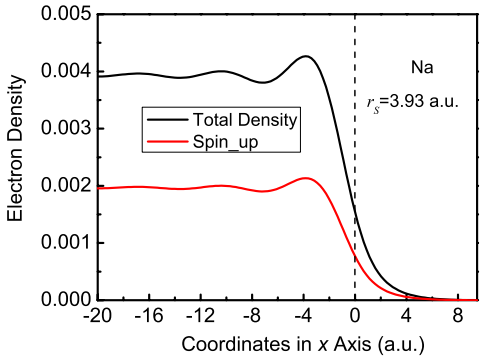

Fig. 1 The total and spin-up electron density near the surface of semi-infinite metal Na

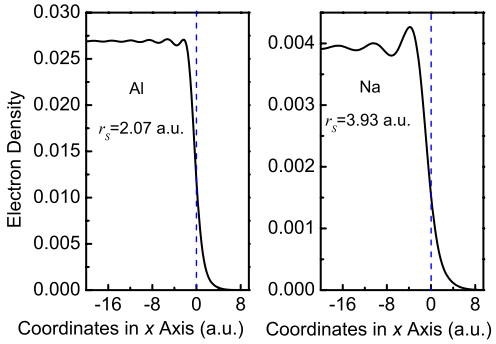

Fig. 2 Comparison of the Friedel oscillation in electron density near the surfaces of Na and Al

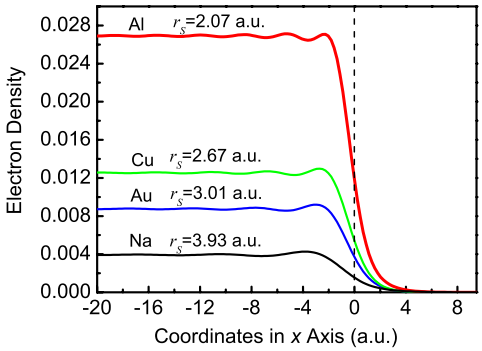

Fig. 3 Self-consistent electron density near the surfaces of semi-infinite metals Na, Au, Cu and Al

charge density for the left/right electrode is represented by r_{SL}/r_{SR}. Three conditions need to be met to determine the electron density distribution n. (i) The system should be neutral (The total charge should be zero). (ii) In the interior of the metal, v_{eff} should approach a constant value. (iii) Friedel oscillations of the electron density near the metal surface should be recovered. For spin-polarized electron density calculation, the relative spin polarization ζ is defined as $\zeta = (n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow) = (n_\uparrow - n_\downarrow)/n$, where $n_\uparrow/n_\downarrow/n$ represents the spin-up/spin-down/total electron density. The spin-up electron density and spin-down electron density can be determined according to $n_\uparrow = (1+\zeta)n/2$ and $n_\downarrow = (1-\zeta)n/2$, respectively. The most widely used PW91-type [14] exchange-correlation potential is applied to the jellium-model program to perform the spin-polarized calculations for a metal surface and a bimetallic-electrode system.

3 Results and discussion

3.1 Electron density near a metal surface

The exponential forms of the electron density distribution in a semi-infinite metal system $n(x) = \overline{n} - \frac{1}{2}\overline{n}e^{\beta}x(x \le 0)$ and $n(x) = \frac{1}{2}\overline{n}e^{-\beta}x(x > 0)$ with $\beta = 1.0$ [15] are used as the initial electron density for the self-consistent calculations.

3.1.1 Electron density near a nonmagnetic metal surface

We perform the spin-polarized calculation for the spin-up and spin-down electrons near a nonmagnetic metal (Na) surface separately. The total electron density and the spin-up electron density are presented in Fig. 1. One can see that the spin-up electron density is exactly half of the total electron density, consistent with the nonmagnetic property of the metal. To test the reliability of the spin-polarized calculation program, we also perform the calculation using the original non-spin-polarized program [4–7]. No difference between the total density calculated from the new and old program can be found, verifying the reliability of the new-developed program. The amplitude of the Friedel oscillation in the electron density near the metal surface is found to be related to r_s value. The Friedel oscillation in the electron density near the surface of semi-infinite Al is compared with that of Na in Fig. 2. One can see that with the increase of the r_s value, the amplitude of the oscillation increases as well. On the other side, in the deep interior of the metal (more than 20.0 a.u., that is, far away from the metal surface), the electron density tends to be a constant, which is consistent with the semi-infinite property of the metal.

The self-consistent total electron density near common metal Na/Au/Cu/Al surface is presented in Fig. 3. The corresponding r_s values of the positive charges of the metals Na, Au, Cu and Al are 3.93 a.u., 3.01 a.u., 2.67 a.u. and 2.07 a.u., respectively. The dashed line in the figure shows the position of the metal surfaces. One can see that in the range of all r_s values we have considered, the electron density decreases exponentially near the metal surface and almost drops to zero at around 8.5 a.u. away from the metal surface. The result suggests that for a pair of bare metallic electrodes with the distance between the two planar electrodes being larger than twice of 8.5 a.u. (i.e., 17.0 a.u.), electrons can hardly transfer from one electrode to the other.

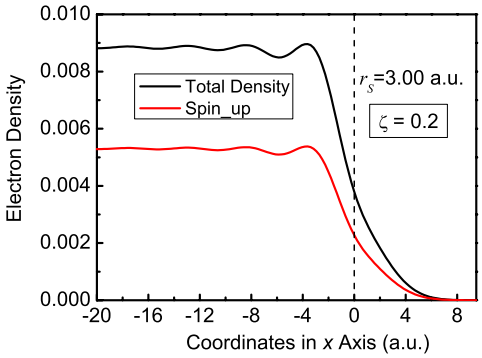

Fig. 4 The spin-up and total electron density near the surface of a semi-metal with spin polarization of 0.2 ($r_s = 3.00$ a.u.)

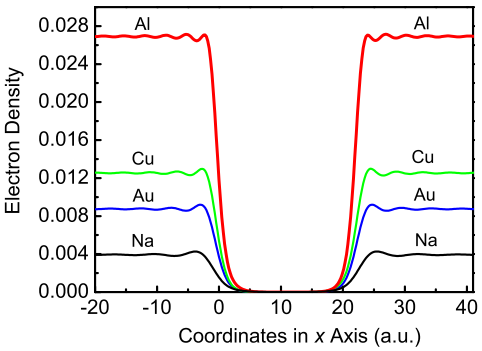

Fig. 5 The electron density of bimetallic-electrode system with the same electrode material Na, Au, Cu, Al. The coordinates of the metal surfaces of the left and right electrode are $x = 0$ and $x = 21.70$ a.u., respectively

3.1.2 Electron density near a magnetic metal surface

We study the electron density near a magnetic metal surface by considering a random r_s with a random spin polarization ζ. As an example, the spin-up and total electron densities near the surface of a semi-infinite metal with $r_s = 3.00$ a.u. and spin polarization $\zeta = 0.2$ are presented in Fig. 4. Any metal surface problem can be treated in the same way by changing r_s and ζ.

3.2 Electron density in a bimetallic-electrode system

We construct a bare bimetallic-electrode system with two electrodes being the same metal Na/Au/Cu/Al and calculate the electron density of the system, shown in Fig. 5. One can see that the electron density presents reasonable symmetry which is consistent with the structural symmetry. A bare bimetallic-electrode system with two different electrodes is also constructed and the electron density of the system is presented in Fig. 6. The spin-up electron density is found to be exactly half of the total density due to the nonmagnetic properties of the electrodes. For comparison, the electron

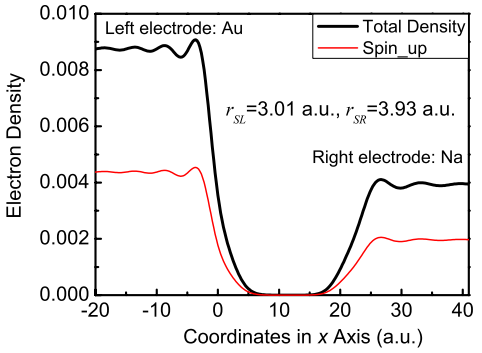

Fig. 6 The electron density in bimetallic-electrode system with the left electrode being Au ($r_s = 3.01$ a.u.) and the right electrode being Na ($r_s = 3.93$ a.u.). The coordinates of the metal surfaces of the left and right electrode are $x = 0$ and $x = 21.70$ a.u., respectively

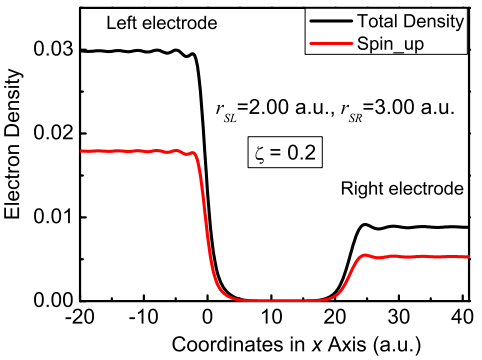

Fig. 7 The total and spin-up electron density in a magnetic bimetallic-electrode system ($r_{SL} = 2.00$ a.u., $r_{SR} = 3.00$ a.u., $\zeta = 0.2$). The coordinates of the metal surfaces of the left and right electrode are $x = 0$ and $x = 21.70$ a.u., respectively

density in a bimetallic-electrode system with a spin polarization of 0.2 is shown in Fig. 7, from which one can see that the spin-up electron density is not half of the total density any more.

4 Conclusion

Spin-polarized self-consistent calculations based on the jellium model are performed for some metal surfaces and some bimetallic-electrode systems. Our work provides a good ground for a future first principles study on spin-dependent metal–molecule–metal tunneling junctions.

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