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RESEARCH ARTICLE

Wave Packet Propagation and Density Functional Theory Investigation For Na-AgCu Interactions

Falah Hassan¹, Batool Daram², Abbas Shwya³

1. Thi-Qar University, College of science, Physics Department

2. Mustansiriyah University, College of science, Physics Department

3. Mustansiriyah University, College of science, Physics Department

abbasalwan@hotmail.com

Abstract

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Key words: WPP Potential models Survival Probability DFT Energy gap DOS Wave Packet Propagation (WPP) method has been used to investigate potential models (jellium and Miller), the logaritms of modulus of the initial electron wave packet at static distance (7 a.u) between Na⁺ and Ag/Cu (jellium and Miller) and survival probability of Na ion close to Ag/Cu in both cases jellium and Miller. Optimization plus frequency, B3LYP, 3-21G basis sets has been carried out at the ground state level by using Density Functional Theory (DFT) to investigate molecular structure, surfaces, contours, infrared spectra, HOMO energies, LUMO energies, Energy gap (E_{σ}) , polarizability and Density Of States (DOS). NaCu₂Ag₄ has energy gap $(E_g=1.1679 \text{ eV})$ which closes to the energy gap of silicon $(E_g=1.2 \text{ eV})$ at absolute zero. Also NaCu₂Ag₄ has the highest value of average polarizability (442.2750 a.u), hence NaCu₂Ag₄ is the highest reactivity nanocluster among the four nanoclusters. Cu2Ag4 has seven peaks, but NaCu2Ag4 has twelve peaks. This difference in number of peaks between these two nanoclusters can easily show influence adding an alkali atom to transition metal nanocluster throughout (Na-Cu) bonds and (Na-Ag) bonds which generate in NaCu₂Ag₄.

1. Introduction:

1.1: Ion Surface Interaction:

When an ion close to a solid surface, the electronic state interact with those of the solid surface and lead to possibility of charge transfer between the ion and the solid surface. This charge transfer has an importance and vital role in a variety different applications. Particularly distortion, adsorption, desorption, implanation, fragmentation of adsorbates, chemical reaction and resonance charge transfer (RCT). One electron transfer between energetically degenerate electronic levels of the ion and solid surface is called resonance charge transfer (RCT). Interaction enable to use the ion scattering as a probe of surface electronic properties. Electron exchange between ion and solid surface can be seen frequently in many scattering experiments between ions and solid surfaces. For example if the incoming particle is (H), the scattered beam may contains (H^+), and if the incoming particle is (Na), the scattered beam may contains (Na^+). Distribution of the scattered particles among the various charged states are strongly rely on the nature of the surface. [1 - 4].

1.2: Basis Sets:

In general the basis set is a collection of vectors which spans a space in which a problem is solved. The basis set in theoretical and computational chemistry is a set of functions which called basis functions. It is functionals in which used to describe the shape of orbitals in atoms. In quantum chemistry the basis set usually refers to the sets of non-

orthogonal one particle functions which is used to build molecular orbitals, in which the molecular orbitals results from linear combination of atomic orbitals. These functions are typically atomic orbitals centered on atoms. The atomic orbital has one electron function. The choice must take accuracy of results and CPU time in account. Molecular orbitals and entire wave functions are created by linear combination of the basis functions and angular functions. Most semi-emperical methods use predefined basis sets. But Ab-initio and DFT calculations require specified basis sets, i.e. in Ab-initio and DFT methods the basis set should specify. Most calculations are done by using existing basis sets [5-8].

1.3: Geometry Optimization:

Geometry optimization is the name for the procedure that attempts to find the configuration of minimum energy of the molecule. The procedure finds the wave function and calculates the energy at starting geometry and then search a new geometry of a lower energy. This is repeated until the lowest energy geometry is found. The procedure calculates the force on each atom by evaluating the gradient (first derivative) of the energy with respect to atomic positions, aiming for rapid convergence to the geometry of the lowest energy. Sophisticated algorithms are then used at each step to select a new geometry. In the final minimum energy geometry, the force on each atom is zero. Naturally, a successive search for a minimum finds a local minimum but not necessarily the lowest. In fact the optimization procedure stops when it finds a stationary point, i.e. a point when the forces resultant on the atoms are zero, and this may be also a saddle point i.e. transition structure. This will occur particularly if the symmetry of the molecule is restricted, it does not allow the program to search the full space of molecular configurational degrees of freedom. It is always a good idea to start a procedure of a geometry optimization calculation with a small basis set and a relatively poor method before the movement of choice for a particular problem. It can then start the final geometry optimization from the geometry selected by the simpler and less accurate approach. During the optimization, also the second derivatives of the energy with respect to atomic coordinates are used. Geometry optimization goals are to find the local minimum structure, the global minimum structure and the transition state structure[9, 10].

2. Wave packet propagation (WPP) Results:

Wave packet propagation method discusses the potential of the surface in two cases, the first is jellium potential and the second is Miller's indices potential (hkl). This means WPP studies the time evolution of an electron wave packet in a compound potential. The wave function $\Psi(r,t)$ represents a solution of time dependent Schrodinger equation. The function $\Psi_a(r)$ stands for the initial wave function $\Psi(r, 0)$. The cylindrical coordinates are used in WPP method (z represents the electron coordinate along the symmetry axis, φ stands for the azimuth angle.

The interaction between the wave function of the projectile and potential models of the surface obey the equation:

$$\begin{aligned} f(r,t+\Delta t) &= f(u,v) + \frac{i\Delta t}{2(\Delta z)^2} [f(u,v+1) + f(u,v-1) - 2f(u,v)] + i\Delta t [V_{e-c}(r_{u,v}) + V_{e-s}(z_v)] f(u,v) \\ &- \frac{i\Delta t}{8x_u^2 (\Delta x)^2} \left[\left(\frac{x_u + \frac{\Delta x}{2}}{x_u + \Delta x} \right) f(u+1,v) + \left(\frac{x_u - \frac{\Delta x}{2}}{x_u - \Delta x} \right) f(u-1,v) \right. \\ &+ 2 f(u,v) \right] & \dots (1) \end{aligned}$$

The electron wave packet autocorrelation function is:

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$$A(t) = \langle \Psi_a(r) | \Psi(r, t) \rangle \qquad \dots (2)$$

By using Laplace transform[11]:

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$$g(\omega) = \frac{1}{\pi} \int_{0}^{\pi} dt \ e^{i\omega t} \ A(t) \qquad \dots (3)$$

$$=\frac{1}{\pi}\int_{0}^{\infty} dt \ e^{i\omega t} \ \langle \Psi_{a}(r)|\Psi(r,t)\rangle \qquad \dots (4)$$

2.1. Potential models:

The wave packet propagation method has been used to investigate Na ion projectile on Ag/Cu surface. The electron wave function interacts with the surface through potential of Ag/Cu surface. The electron surface distance is measured from the image surface reference plane z_o . WPP method depends on time dependent Schrodinger equation which needs the following:

- 1) Potential of the projectile
- 2) Potential of the surface in two cases
- a- Jellium potential
- b- Miller indices (hkl) potential

One must note hkl potential represents the real potential which is periodic along the z-axis inside the metal. Miller potential is independent on the coordinate that are parallel to the surface, but Jellium potential stands for the potential outside the metal. The the potential of Na ion projectile can be represented by an exponential function.

for Jellium Ag/Cu surface: -270 ($1 - e^{-z}$)

$$V_{e-s}(z) = \frac{-270(1-e^{-z})}{z^2} - 4.16 \qquad z > 5.966 \qquad \dots (5)$$

And for Ag/Cu *hkl* potential one can write:

 $\begin{aligned} V_{e-CuAg}(z) &= 2\sin z^a - 10 & z < 0 & \dots(6) \\ V_{e-CuAg}(z) &= 0.2 \, z + 2\sin(\sin(0.7 \, z^b)) - 10 & 5.966 > z \ge 0 & \dots(7) \end{aligned}$

a, b: arbitrary constants. From the equations (5, 6, 7) one can see the potential depends only on z.

In this study the surface potential in two cases Miller and Jellium have been investigated for Ag/Cu surface. Matlab program has been used to investigate potential in both cases Miller and Jellium [12, 13].



The surface potential for Ag/Cu in both cases Miller and jellium

2.2. Wave packet propagation as a function of time:

Matlab program has been carried out to investigate the wave packet propagation as a function of time in the static case for positive sodium ion (Na⁺) on Ag/Cu in two cases jellium and Miller. The static calculations of the electron coordinates z and ρ (normal and parallel to Ag/Cu surface) at a fixed distastance (z=7 a.u) from the surface and times (0 a.u, 45 a.u, 120 a.u, 350 a.u, 550 a.u, 750 a.u and 1400 a.u). The origin of the electronic coordinates is placed at the center of (Na⁺) ion. This method is used in reference [14].



Figure (2) The wave function for positive sodium ion (Na^+)



Figure (3) Contour for Cu/Ag surface at 0 a.u at distance 7 a.u from the surface



Figure (4) Contours for Ag/Cu surface in jellium case at distance 7 a.u from the surface





Contours for Ag/Cu surface in Miller case at distance 7 a.u from the surface

2.3. Survival probability:

The survival probability gives the probability of ion survival close to the surface, and it can be found from the relation [15]:

 $P(t) = |A(t)|^2$

Matlab program has been used to investigate survival probability for Ag/Cu surface in both cases Miller and Jellium potentials in which the survival probability depends on the time as the relation (4)



Survival probability for Ag/Cu in two cases Jellium and Miller full line stands for Jellium, dashed line stands for Miller

3. Density Functional Theory (DFT) Calculations:

3.1. Molecular Structure:

Optimization plus Frequency has been carried out to optimize Cu_2Ag_4 nanocluster, Cu_4Ag_2 nanocluster, $NaCu_2Ag_4$ nanocluster and $NaCu_4Ag_2$ nanocluster. DFT has been used at 3-21G and B3LYP basis sets at the ground state with Gaussian 09 software package. This technique has been used in reference [16].





3.2. Surfaces and contours:

Surfaces and contours at electrostatic potential (ESP) have been carried out by using molecular orbitals for HOMO and LUMO electronic states for Cu_2Ag_4 nanocluster, Cu_4Ag_2 nanocluster, $NaCu_2Ag_4$ nanocluster and $NaCu_4Ag_2$ nanocluster. This method which investigates surfaces and contours has been used in reference [17].



Contours for Cu₂Ag₄, Cu₄Ag₂, NaCu₂Ag₄, NaCu₄Ag₂.

3.3. Infrared spectra:

The harmonic vibrational frequencies have been investigated for Cu_2Ag_4 nanocluster, Cu_4Ag_2 nanocluster, $NaCu_2Ag_4$ nanocluster and $NaCu_4Ag_2$ nanocluster at ground state, B3LYP and 3-21G basis sets. There are two types of stretching variations, symmetric and asymmetric. The symmetric stretching is happening when the same atoms vibrate in the same phase, and the asymmetric stretching is happening when the bonds vibrate in different phases. The method which is used to investigate infrared spectra is also used in the reference [18].



Infrared spectra for Cu₂Ag₄, Cu₄Ag₂, NaCu₂Ag₄, NaCu₄Ag₂.

3.4. Electronic states and Energy gap (E_g):

HOMO and LUMO energies represent the electronic states.

HOMO : High Occupied Molecular Orbital

LUMO : Low Unoccupied Molecular Orbital

The difference between HOMO and LUMO energies give the energy gap (E_g) as follows: [19]

$$E_{\rm g} = E_{HOMO} - E_{LUMO} \qquad \dots (9)$$

system	$E_{HOMO}(eV)$	$E_{LUMO}(eV)$	$E_{\rm g}(eV)$
Na	-3.4783	-0.5586	2.9197
Cu_2Ag_4	-4.7677	-2.3273	2.4404
Cu ₄ Ag ₂	-4.4777	-2.3564	2.1213
NaCu ₂ Ag ₄	-3.4897	-2.3218	1.1679
NaCu ₄ Ag ₂	-4.2777	-2.1344	2.1433

Table (1): Electronic states and Energy gap for Cu₂Ag₄, Cu₄Ag₂, NaCu₂Ag₄, NaCu₄Ag₂.

3.5. Polarizability(α):

Polarizability describes the ability of molecule for polarization. Polarizability determines the linear response of the electron density in the presence of an infinite seminal electric field F, and stands for a second order variation in the energy.

$$\alpha = -\left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right)_{a,b} = x, y, z \qquad \dots (10)$$

The mean polarizability $\langle \alpha \rangle$ is evaluated by using the equation [20]:

$$<\alpha>=\frac{1}{3}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz}) \qquad \dots (11)$$

Where α_{xx} , α_{yy} and α_{zz} are the eigen values of the polarizability tensor. Polarizability signifies the dynamical response of a bound system to external fields and supplies insight into a molecules internal structure.

system	α_{xx}	α_{yy}	α_{zz}	$\langle \alpha \rangle$
Cu ₂ Ag ₄	153.396	306.403	324.864	261.5543
Cu_4Ag_2	137.899	332.526	285.241	251.8887
NaCu ₂ Ag ₄	715.865	367.591	243.369	442.2750
NaCu ₄ Ag ₂	327.118	336.882	249.753	319.5843

Table (2): Polarizability for Cu₂Ag₄ and Cu₄Ag₂.

3.6. Density of states (DOS):

In solid state and condensed matter physics, the density of states(DOS) of a system describes the number of states per interval of energy at each energy level that are available to be occupied. A high density of state at a specific energy level means that there are many states available for occupation. A density of state zero means no state can be occupied at the energy level. In general, a density of state is an average over the space and time domains are occupied by the system. In quantum mechanics systems, waves, or wave-like particles can occupy modes or states with wavelengths and propagation directions dictated by the system often only specific states are permitted. In some systems, the interatomic spacing and the atomic charge of the material allows only electrons of certain wavelengths to exist. In other systems, the crystalline structure of the material allows waves to propagate in one direction while it suppresses the wave propagation in another direction. Thus, it can happen that many states are possible at a specific wavelength at this associated energy, while no states are available at other energy levels. This distribution is characterized by the density of states. Density of states can be investigated for electrons, photons and phonons according to quantum mechanics. In general, density of states influenced by topological properties of the system [21 - 24].



Density of states for Cu_2Ag_4 , Cu_4Ag_2 , $NaCu_2Ag_4$, $NaCu_4Ag_2$.

4. Discussion:

Figures (1) describe the surface potential for Ag/Cu surfaces in both cases jellium and Miller. The work function for Cu(111) is close to (4.6 eV), while the work function for Ag(111) is close to (4.5 eV). One can note the ionization energy is high for the ground state level, while the ionization energy for the resonant first excited level is low. Hence, the probability of transfer an electron from the surface will be high for the ground state level. The negative direction refers to the atoms inside the surfaces i.e. Miller surfaces. The positive direction denotes to the vacuum. This means the atoms are out the surfaces i.e. jellium surfaces. In the figure, sine waves gives Miller potential, but exponential function gives eithier jellium or Miller. Jellium surface depends on free electron model i.e. each atom is found individual and has no interaction with the neighbor atoms. Miller potential assumes each atom interacting with the neighbor atoms i.e. Miller potential is a periodic potential. This consequence in general agreement with solid state physics [25].

Figures (3, 4, 5) show contours for Ag/Cu jellium surface and Ag/Cu(111) surface. Contours give the spatial distribution with the surface. Before discussing these figures, one must know the study gives behavior of the interaction and possibility to happen. The wave function represents solution of time dependent Schrodinger equation. These figures explain influence the surfaces by the period of time at static distance z. The surfaces result from logarithms of modulus of the initial electron wave packet at static distance (7 a.u) between Na⁺ ion and Ag/Cu surface at different periods (0 a.u, 45 a.u, 120 a.u, 350 a.u, 550 a.u, 750 a.u and 1400 a.u) in two cases jellium and Miller. At (0 a.u) i.e before the interaction one can note that propagation of wave functions uniform and this is very clear in the contour diagram. Hence, one can say there is no distortion in the propagation wave function before the interaction. At (45 a.u) one can see small distortion in contour diagram. At (120 a.u) the distortion in wave functions look very clear. This distortion in the propagation wave function continues until the period (750 a.u). At (750 a.u) one can watch obviously the propagation wave function form approximately looks fixed. But it is very clearly that the propagation becomes deeper with increasing the period of time. In jellium potential case, the propagation reduces with the parallel direction of the surface. In Miller surface case, the propagation increases with the parallel direction of the surface. The distortion in the propagation wave function proves that resonance charge transfer happens between Na^+ and the surface. One can say an electron in Na^+ finds its image on Ag/Cu(111) surface. This means there is new orbital generates when Na⁺ ion is close to the surface. It is very necessary to know that image state happens under the conduction band because the resonance, while surface state is a place to find an electron up the valence band because of the first three layers of the solid material. The method which is used to investigate the wave function as a function of time interaction in this study is also used in references [26 - 28].

Figures (6) describe the ion survival probability for Ag/Cu and Ag/Cu(111). The wave function has normalization before the interaction. When the probability equals to 1, this means the wave function of Na⁺ has no interaction with the surface in both cases jellium and miller. Whereas the probability drops under 1, this means there is an interaction between Na⁺ ion and the surface. This interaction depends on the drop value, and may be an oscillation happens because of Pauli's exclusion principle. After long time periods, the interaction probability is stable because of the charge transfers. Wave packet propagation method is suitable to describe one electron at certain period. The time propagation may cause inaccuracy because of another electronic transition may happen and affect on resonance charge transfer. Na⁺ ion survival probability depends on the autocorrelation function A(t) between the ion and the surface. In jellium cases, the ion survival probability near the surface decays faster than Ag/Cu(111) cases. This is because Miller model gives real wave packet propagation. The consequence in this study are in good agreement with reference [29].

Figures (11) describes IR spectra for Cu_2Ag_4 nanocluster, Cu_4Ag_2 nanocluster, $NaCu_2Ag_4$ nanocluster and $NaCu_4Ag_2$ nanocluster respectively. IR spectra gives harmonic vibrational frequencies, torsion vibrations appears at low frequencies, the number of atomic modes depend on the number of the atoms in the nanocluster. Each value or each range stands for vibration mode, the vibration either elastic or inelastic. In the figures, it has been observed peaks, and these peaks refer to the bonds between atoms. Someone can see influence Cu_2Ag_4 and Cu_4Ag_2 nanoclusters by adding sodium atom throughout (Na-Cu bonds) and (Na-Ag bonds) which generate in $NaCu_2Ag_4$ and $NaCu_4Ag_2$ nanoclusters. For example, Cu_2Ag_4 has seven peaks, but $NaCu_2Ag_4$ has twelve peaks. This variation in number of peaks between these two nanoclusters can simply explain influence adding an alkali atom to transition metal nanoclusters. The method which is used to study IR spectra in this study is also used in reference [30].

Tables (1) stands for the electronic states in (eV) for Cu₂Ag₄ nanocluster, Cu₄Ag₂ nanocluster, NaCu₂Ag₄ nanocluster and NaCu₄Ag₂ nanocluster respectively. HOMO energies for Cu₂Ag₄ and Cu₄Ag₂ nanoclusters are higher than the HOMO energy for sodium atom. Therefore the electrons will release to the unoccupied orbitals, hence one can consider Cu₂Ag₄ and Cu₄Ag₂ as acceptors, sodium as donor. The energy gap of NaCu₂Ag₄ close to

the energy gap of semiconductors. NaCu₂Ag₄ has energy gap (1.1679 eV) and this value of energy gap closes to energy gap of silicon which has energy gap (1.2 eV) at absolute zero. The method which is used to find the electronic states and energy gap in this study is also used in references [31 - 33].

Table (2) stands for polarizability for Cu_2Ag_4 nanocluster, Cu_4Ag_2 nanocluster, $NaCu_2Ag_4$ nanocluster and $NaCu_4Ag_2$ nanocluster respectively. One can see from these tables that adding an alkali atom such as sodium to transition nanocluster increases the value of average polarizability. The nanocluster which has higher average polarazibility has higher reactivity. Hence $NaCu_2Ag_4$ is the highest reactivity nanocluster among the four nanoclusters because it has the highest value of average polarizability (442.2750 a.u). The polarizability is very important property. It gives a sight about internal structure for the molecule. In general, the average polarizability is also used in reference [34].

Figures (12) stands for density of states for Cu_2Ag_4 nanocluster, Cu_4Ag_2 nanocluster, $NaCu_2Ag_4$ nanocluster and $NaCu_4Ag_2$ nanocluster respectively. A high density of state at a certain energy level means that there are many available states being occupied. When the density of state equals to zero, that means there is no available energy level being occupied. The local vibrations result from distortion of the original system. It is called local density of state (LDOS). If the density of state for an undistributed system is zero, LDOS will not probably be zero. This is because the local potential is found. When the electron energy increases, the density of state increases. Many states become available to be occupied. The topological properties also affect on density of states affect small when sodium atom is added to Cu_2Ag_4 and Cu_4Ag_2 . This means there are many orbitals have been generated. This results is in general agreement with solid state physics [35].

Conclusions:

One can see from countours, in jellium potentials the propagation reduced with the parallel direction of the surface, while in Miller surfaces the propagation increases with the parallel direction of the surface. The distortion in the propagation wave function proves that resonance charge transfer happens between Na⁺ and the surface Ag/Cu throughout the distortion in contours one can concludes resonance charge transfer has been happened when Na⁺ is close to the surface. This property is very beneficial in ion formation and sensors. In jellium case, the ion survival probability near the surface decays faster than these for Ag/Cu(111) case. This is because Miller model gives real wave packet propagation. The molecular structure, surfaces and contours can be investigated for Cu₂Ag₄, Cu₄Ag₂, NaCu₂Ag₄ and NaCu₄Ag₂, hence one can concludes Gaussian program is found stationary point through geometry optimization procedure. New peaks appear in IR spectra when sodium atom is added to the nanoclusters, i.e. new bonds are formed between sodium atom and atoms of the nanoclusters. The energy gap for NaCu₂Ag₄ close to the energy gap of semiconductrs. NaCu₂Ag₄ has energy gap equal to (1.1679 eV) which closes to the energy gap of silicon which has (E_g=1.2 eV) at absolute zero. This is very important in solar cells and electronic devices such as detectors, transistors, integrated circuits, etc. Also NaCu₂Ag₄ has the highest value of average polarizability (442.2750 a.u), hence NaCu₂Ag₄ is the highest reactivity among all nanoclusters in this study nanocluster.

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References:

[1] A.A. Saleh, V. Shutthanandan, N.R. Shivaparan, R.J. Smith, T.T. Tran and S.A. Chambers, *Phys. Rev. B*, 56, 9841 (1997).

[2] A. Murgaza, A. Mascaraque, V. Pérez-Dieste, V. Repain, S.Rousset, F. J. García de Abajo, and J. E. Ortega, Phys. Rev.Lett. 87, 107601 (2001).

[3] F. Schiller, M. Ruiz-Osés, J. Cordón, and J. E. Ortega, Phys. Rev. Lett. 95, 066805 (2005).

[4] A. G. Borisov, J. P. Gauyacq and S. V. Shabanov, Surf. Sci., 487, 243 (2001).

[5] W. Hehre, L. Radom, P. Schileyer and J. Pople, "Ab-initio molecular orbital theory", John Wiely and Sons, 1986.

[6] Ali A. M., "Investigations Of Some Antioxidant Materials By Using Density Functional And Semiempirical Theories", P.hD. Thesis, University of Basrah, College of Science, Department of Physics, 2009.

[7] C. David Sherril, "A Brief Review of Elementary Quantum Chemistry", Georgia Institute of Technology, 2001.

[8] Efthimios Kaxiras, "Atomic and Electronic Structure of Solid", Cambridge University Press, New York, USA, 2003.

[9] M. J. Frisch, G.W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G.Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hartchain, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T.Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J.Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V.G. Zakrzewski, G. A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A. D. Daniels, O.Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, "Gaussian 09", revision A. 1, Gaussian, Inc., Wallingford CT, (2009).

[10] Gaussian09 Tutorial "An introduction to computational chemistry using G09 and Avogadro software, Anna Tomberg.

[11] A. G. Borisov, D. Teillet . Billy, and J. P. Gauyacq, Phys. Rev. Lett., 68. 2842 (1992).

[12] A. G. Borisov. Phys. Rev. B, Vol.59, No.1615, April (1999).

[13] M. C. Desjonque`res and D. Spanjaard, *Concepts in Surface Physics*, Springer Series in Surface Sciences, Vol. 30 ~Springer-Verlag, Berlin, 1993.

[14] Borisov. Resonant charge transfer in ion-metal surface collisions: Effect of a projected band gap in the H2-Cu(111) system.

[15] Charge exchange in atom, ion and cluster surface scattering process, wave packet propagation configuration and rate equation methods, Ph.D thesis, F. H. Hanoon Al Asady, Basrah university.

[16] Koray Sayin, Duran Karakas, Journal of New Results in Science 8 (2015) 01-12.

[17] Koray Sayin, Duran Karakas, Indian Journal Chem, Sec A, April 2013.

[18] Mohsin K. AL Khaykanee1, H. Ibrahim Aboud, Int. J. Pure Appl. Sci. Technol., 15(1) (2013), pp. 1-13.

[19] H. Ibrahim Aboud, British Journal of Science, September 2012, Vol. 6 (2).

[20] A.M. Ali, Investigations of some antioxidant materials by using density functional and semiempirical theories,

PhD. Thesis, University of Basra, College of Science, Department of Physics, (2009).

[21] Introduction to Solid State Physics", Charles Kittel.

[22] J.S Blakemore, 1969, Solid State Physics, Philadelphia: W. B. Saunders.

[23] J. Ziman, 1972, Principles of the Theory of Solids, second edition, Cambridge: Canbridge University Press.

[24] dachi T. and Sunada. T (1993). "Density of states in spectral geometry of states in spectral geometry". *Comment. Math. Helvetici* 68: 480–493.

[25] J. D. Patterson, 1971, Introduction to the Theory of Solid State Physics, Reading, Mass. Addison-Wesley

[26] A. G. Borisov, A. K. Kazansky, and J. P. Gauyacq, Phys.Rev. B, 59, 16 10 935 (1999).

[27] A. Borisov, D. Sanchez-Portal, R. Diez Muino, P.M. Echenique, Chem. Phys. Lett. 387 (2004) 95.

[28] A.G. Borisov, D. Sa'nchez-Portal, R. Di'ez Muin'o, P.M. Echenique, Chem. Phys. Lett. 393 (2004) 132

[29] J. P. Gauyacq and A. G. Borisov, J. Phys.: Condens. Matter 10, 6585, 1998

[30] Int. J. Pure Appl. Sci. Technol., 15(1) (2013), pp. 1-13, Mohsin K. AL-Khaykanee, and H. Ibrahim Aboud.

[31] "Effect of Some Electron Donor and Electron Acceptor Groups on Stability of Complexes According to the Principle of HSAB", Journal of New Results in Science, Number: 4, Year: 2014, Pages: 82-89.

[32] "Copper nanoclusters: Synthesis, characterization and properties", LU YiZhong1,2, WEI WenTao1,3 and CHEN Wei1.

[33] "Density Functional Theory investigation of the Physical Properties of Dicyano Pyridazine Molecules", Fouad N. Ajeel¹, Alaa M. Khudair², Anees A. Mohammed³, "*International Journal of Science and Research"*, volume. 4, 4 issue, 1 Janary 2015.

[34] Density Functional Theory Calculations for Nitro Benzene Molecules Group, H. Ibrahim Aboud

[35] F. C. Brown, 1967, The Physics of Solids, New York: W. A. Benjamin.