

Effect of adatom-phonon interaction on parameters of single walled carbon nanotube

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Double time Green function technique and Zubarev equation of motion approach have been employed. The modified dependence with $\langle n_{\alpha\sigma} \rangle$ and chemisorption energy (ΔE) with radius of single walled carbon nanotube (SWCNT) was estimated. We considered HF approximation to decouple higher order Green function and found that the inclusion of adatom-phonon interaction, change the surface parameters. The comparison of theoretical predication and experimentally observed value indicates to study in detail from the first principle.

Keywords: Adatom-phonon, Nanotube, Carbon nanotube, Green function technique

1 Introduction

By inclusion of adatom-phonon¹⁻³ interaction to the Anderson Hamiltonian⁴ to describe the surface properties of the system under reference it was found it's direct dependence on radius of carbon nano-tube particularly single walled carbon nano tube (SWCNT) with various surface parameters like occupation number of Adatoms and chemisorption energy⁵⁻⁹. The Anderson model⁴ which is one of the most challenging problem of 20th century Physics was subsequently applied to theory of chemisorption by Newns⁵ since then jointly goes by the name of Anderson Newns model. There are two powerful techniques to study the surface phenomenon of chemisorption viz. (i) Zubarev double time Green function technique (ii) density functional technique within the Hamiltonian formalism.

After obtaining the expression of Green function one can find out (i) localized energy (ii) chemisorption energy (iii) occupation number (iv) chemisorption function (v) work function and many other allied surface parameters via density of state.

Keeping in view of the accuracy of the above techniques to study the chemisorption theory and its application on nanotubes we believe that this work will lays the ground work for the effect of adatoms to carbon nano tubes.

Basing on the Green function technique by adopting suitable model Hamiltonian¹⁰⁻¹², the density of states of surface adatoms has been calculated which is applied to carbon nanotubes to find out:

(i) Adatoms density of states for semiconducting and metallic single walled carbon nanotube; (ii) Chemisorption energy of single hydrogen adsorbed on the zig-zag SWCNTS with reference to radius of the nanotubes and many other surface parameters;

2 Theoretical Formulation

A phase transition with changing temperature and with changing degree of coating has been found in films adsorbed on metal surface, which greatly differ from one another. The structure and the electronic states of the adsorbed films on the metal surfaces can be studied by analyzing such phase transitions, as alterations of the electronic state of all the adsorbed atoms accompany such phase transitions. Homogenous electronic state of the adsorbed atom with the same charge changes to a state in which the charge changes from one adsorbed atom to another due to interactions between them. The phase transitions in an adsorbed layer on the metal surface depend on both the interaction of the adsorbed atoms with one another and also on the adatom-phonon¹³⁻¹⁵ interaction. It is therefore, significant to study the effects of adatom-phonon interaction on the electronic states of the adsorbed atoms on the metal surface. Doyen and Grimley¹⁶ have illustrated how multi-phonon processes which can dominate in desorption by considering gas atom-phonon interaction. Shinjo *et al.*¹⁷ have calculated the effects of the image force and adatom-phonon interactions to study the effect of multi-valency of adatoms on the metal surface. Other

similar effects are calculated to study the structural and electronic alterations of the adatoms on the metal surface. We, therefore, calculate the effect of adatom-phonon interaction on the chemisorption energy of the adsorbed atoms and the occupation number. The corresponding Hamiltonian may be written as:

$$H = \sum_{\sigma} E_A n_{A\sigma} + U n_{A\sigma} n_{A\bar{\sigma}} + \sum_{k\sigma} E_k n_{k\sigma} + \sum_q \omega_q b_q^+ b_q + \sum_k \left\{ V_{Ak} C_{A\sigma}^+ C_{k\sigma} + V_{Ak}^+ C_{A\sigma} C_{k\sigma}^+ \right\} + (\sum_{\sigma} n_{A\sigma} - n_{A1}) \sum_q g_q (b_q^+ + b_q) \quad \dots (1)$$

where n_{Ai} stands for the number of adatoms when adatoms are neutral $n_{Ai} = 0, 1, 2$. Kratsov and Malshukov¹⁸ have also considered the widely accepted Anderson Hamiltonian along with the dependence of the energy of the electron localized on the adatom level on the small displacement of the adsorbed atom in the direction perpendicular to the metal surface. They have calculated the average occupation numbers $\langle n_{A\sigma} \rangle$ of the adsorbed atoms, and approximated the two-particle interaction $U n_{A\sigma} n_{A\bar{\sigma}}$ by using the Hartree-Fock approximation¹⁶⁻¹⁸. They also neglected the contribution due to non-diagonal terms as their contribution to the self-energy part of the adatom Green's function is small as compared to U . This is, however, good when the adatom lattice constant is small, otherwise non-diagonal terms of the adatom Green's function are to be considered, which reduce the indirect interaction.

In the present paper, we calculate the chemisorption energy and occupation number with respect to radius by using the Anderson Hamiltonian first without adatom-phonon contribution and then by modifying the Hamiltonian by considering the displacement of the adatom.

3 Methodology

Among the existing theoretical techniques, the method of Zubarev double time Green's function, local density function¹⁹ (LDF) formalism and Feynman Diagram²⁰⁻²¹ technique are the powerful mathematical tools of the Quantum field theoretical models with Hamiltonian approach. The former methodology determines the excitation spectrum through its analytic properties in the complex energy plane and consequently leads to general expression for experimentally measured quantities such as electrical conductivity and magnetic susceptibility. Further,

another important property of the above method is that the Green functions are related, via the fluctuation-dissipation theorem to time correlation functions which determine the average needed to discuss properties of the ground state of the system. When we set up an equation of motion for the corresponding Green's function by using Zubarev formula, higher order Green's functions will appear and the system of equations does not close. One can in turn write down the equations of motion of the new Green's functions, thus, obtaining Green's functions of still higher order. To truncate the infinite hierarchy of differential equations, one can use suitable decoupling approximations which reduce higher order Green's function to lower order Green's function and help in solving them to obtain expressions for required experimental parameters.

4 Theoretical Formulation with Anderson Model

The model Hamiltonian is given by

$$H = \sum_{k,\sigma} E_k n_{k\sigma} + \sum_{\sigma} E_a n_{a\sigma} + \sum_{k,\sigma} \left[V_{ka} C_{k\sigma}^+ C_{a\sigma} + h.c. \right] + U n_{a\uparrow} n_{a\downarrow} \quad \dots (2)$$

where $C_{k\sigma}^+$ ($C_{a\sigma}^+$) is the electron creation operator for the state $|k\rangle$ with spin σ and energy ϵ_k of the conduction electron in the metal (for the orbital $|a\rangle$ of the adsorbate with spin σ and energy ϵ_a), $n = C^+ C$, V_{ka} is the matrix element of hybridization between the conduction electron and the electron on adsorbate. The last term represents the intra-atomic Coulomb interaction for two electrons on the adsorbate. The quantities ϵ_a , V_{ka} and U are the functions of the coordinate of the adsorbate measured from the surface. The quantity we want to calculate is the single particle Green's function of the adsorbate:

$$G(E) = \left\langle \left\langle C_{a\sigma} : C_{a\sigma}^+ \right\rangle \right\rangle_E \quad \dots (3)$$

By obtaining the expression of above adatom Green function we can find occupation number and chemisorption energy by using the following standard formula as follows:

(a) Occupation Number²²⁻²⁵ :

$$\langle n_{a\bar{\sigma}} \rangle = -2 \int_{-\infty}^{E_F} dE \text{Im} G_{aa}(E) \quad \dots (4)$$

(b) *Chemisorption energy*²⁶⁻²⁸

$$\Delta E = \int_{-\infty}^{E_F} \rho(E) E dE - E_a - U n_a^2 \quad \dots (5)$$

from the adatom Green function, the concerned density of states can be found out by the following formula:

$$\rho_{aa}^\sigma(E) = -\frac{1}{\pi} \text{Im} G_{aa}^\sigma(E) \quad \dots (6)$$

Case I – From density of states the occupation number of adatoms can be estimated within the framework of Anderson model as follows :

$$\langle n_{a\sigma} \rangle = \int_{-\infty}^{\infty} \rho_{aa}(E) \frac{E_c^2}{E^2 + E_c^2} dE + \delta_{v,\pm} \langle n_{a\sigma} \rangle_{loc} \quad \dots (7)$$

Case II – and the Chemisorption energy

$$\Delta E^{I\sigma} = E_{loc}^\sigma + \frac{1}{\pi} \int_{-\infty}^{ef} \left(\frac{E_c}{E + E_c} \right) \tan^{-1} \times \left[\frac{\Delta(E)}{E - E_{a\sigma} - \wedge_a(E)} \right] dE \quad \dots (8)$$

Where

$$G_{aa}^\sigma(E) = \left[E - E_{a\alpha} - \sum_{aa}^\sigma(E) \right]^{-1} \quad \dots (9)$$

where $\sum_{aa}^\sigma(E)$ is the one electron self energy and it can be resolved into two parts namely;

$$\sum_a^{(v)}(E) = \wedge_a^{(v)} - i\Delta_a^{(v)}(E) \quad \dots (10)$$

and E_{loc}^σ is the localized energy i.e. the energy required to localize on electron in the orbital $|1\rangle$.

4.1 Calculation with Anderson Hamiltonian with adatom-phonon interaction

Using Eq. (1) for the Hamiltonian, the equation of motion for the Green's function, $G_{AA}(E)$, can be simplified to:

$$(E - E_A) \langle\langle C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E = \frac{1}{2\pi} + U \langle\langle C_{A\sigma} n_{A\bar{\sigma}} | C_{A\sigma}^+ \rangle\rangle_E$$

$$+ \sum_k V_{Ak} \langle\langle C_{k\sigma} | C_{A\sigma}^+ \rangle\rangle_E + \sum_q g_q \langle\langle C_{A\sigma} (b_q + b_q^+) | C_{A\sigma}^+ \rangle\rangle_E \quad \dots (11)$$

we get additional higher-order Green's functions which correspond to adatom-phonon interactions like $\langle\langle C_{A\sigma} b_q | C_{A\sigma}^+ \rangle\rangle_E$ and $\langle\langle C_{A\sigma} b_q^+ | C_{A\sigma}^+ \rangle\rangle_E$. To solve the Green's function, $G_{AA}(E)$, we simplify the adatom-phonon Green's functions as follows:

$$(E - E_A - U \langle n_{A\bar{\sigma}} \rangle - \omega_{q\lambda}) \langle\langle b_\sigma C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E = \sum_k V_{Ak} \langle\langle b_q C_{k\sigma} | C_{A\sigma}^+ \rangle\rangle_E + \sum_q g_q \langle\langle b_q b_q^+ \rangle\rangle \langle\langle C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E + g_q \langle (\sum_\sigma n_{A\sigma} - n_{A1}) \rangle \langle\langle C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E, \quad \dots (12)$$

$$(E - E_A - U \langle n_{A\bar{\sigma}} \rangle + \omega_{q\lambda}) \langle\langle b_\sigma^+ C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E = \sum_k V_{Ak} \langle\langle b_\sigma^+ C_{k\sigma} | C_{A\sigma}^+ \rangle\rangle_E + \sum_q g_q \langle\langle b_q^+ b_q \rangle\rangle \langle\langle C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E - g_q \langle (\sum_\sigma n_{A\sigma} - n_{A1}) \rangle \langle\langle C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E. \quad \dots (13)$$

Here we use following decoupling approximation for the higher-order Green's functions:

$$\langle\langle b_q C_{A\sigma} (b_q + b_q^+) | C_{A\sigma}^+ \rangle\rangle_E \approx \langle\langle b_q b_q^+ \rangle\rangle \langle\langle C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E, \\ \langle\langle b_q C_{A\sigma} n_{A\bar{\sigma}} | C_{A\sigma}^+ \rangle\rangle \approx \langle n_{A\bar{\sigma}} \rangle \langle\langle C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E, \\ \langle\langle (\sum_\sigma n_{A\sigma} - n_{A1}) C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E \approx \langle (\sum_\sigma n_{A\sigma} - n_{A1}) \rangle \langle\langle C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E. \quad \dots (14)$$

The Green's function $\langle\langle b_q C_{k\sigma} | C_{A\sigma}^+ \rangle\rangle_E$ may be similarly obtained as:

$$(E - E_k - \omega_{qi}) \langle\langle b_q C_{k\sigma} | C_{A\sigma}^+ \rangle\rangle_E = V_{Ak}^+ \langle\langle b_q C_{A\sigma} C_{A\sigma}^+ \rangle\rangle_E + g_q \langle (\sum_\sigma n_{A\sigma} - n_{A1}) \rangle \langle\langle C_{k\sigma} | C_{A\sigma}^+ \rangle\rangle_E \quad \dots (15)$$

Substituting the expression for $\langle\langle C_{k\sigma} | C_{A\sigma}^+ \rangle\rangle$ we get:

$$\langle\langle b_q C_{k\sigma} | C_{A\sigma}^+ \rangle\rangle_E = \frac{V_{Ak}^+}{E - E_k - \omega_{q\lambda}} + \frac{g_q \langle (\sum_{\sigma} n_{A\bar{\sigma}} - n_{Ai}) \rangle V_{Ak}^+}{(E - E_k - \omega_{q\lambda})(E - E_k)} \langle\langle C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E \dots (16)$$

Substituting Eq. (16) into Eq. (14) and also using a suitable decoupling approximation, we get:

$$\begin{aligned} \langle\langle b_q C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E &= \\ &= \frac{1}{E - E_A - U \langle n_{A\bar{\sigma}} \rangle - \sum_k \frac{V_{Ak}^2}{E - E_k - \omega_{q\lambda}} - \omega_{q\lambda}} \\ &\times \left\{ \sum_q g_q \langle b_q b_q^+ \rangle + g_q \langle (\sum_{\sigma} n_{A\sigma} - n_{Ai}) \rangle \right. \\ &\left. + \sum_k \frac{V_{Ak}^2}{E - E_k} g_q \frac{\langle (\sum_{\sigma} n_{A\sigma} - n_{Ai}) \rangle}{E - E_k - \omega_{q\lambda}} \right\} \\ \langle\langle C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E &\dots (17) \end{aligned}$$

A similar expression can be obtained for the Green's function, $\langle\langle b_q^+ C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E$. We, however, find higher-order scattering terms which can be neglected without any appreciable error in our results. Therefore Eq. (11) leads to the following simplified expression:

$$\begin{aligned} \left(E - T_A - \frac{F_{\bar{\sigma}} U}{E - T_A - U + F_{\bar{\sigma}}} - M_{q\lambda}^{ph}(E) \right) \\ \langle\langle C_{A\sigma} | C_{A\sigma}^+ \rangle\rangle_E = \frac{1}{2\pi} \left\{ 1 + \frac{U \langle n_{A\bar{\sigma}} \rangle}{E - T_A - U + F_{\bar{\sigma}}} \right\} \dots (18) \end{aligned}$$

where we substitute

$$\begin{aligned} M_{q\lambda}^{ph}(E) = \\ \sum_q g_q^2 \left\{ \frac{\langle b_q b_q^+ \rangle + \langle (\sum_{\sigma} n_{A\sigma} - n_{Ai}) \rangle}{E - T_A - U \langle n_{A\bar{\sigma}} \rangle - \sum_k \frac{V_{Ak}^2}{E - E_k - \omega_{q\lambda}} - \omega_{q\lambda}} \right. \\ \left. \frac{\langle b_q^+ b_q \rangle - \langle (\sum_{\sigma} n_{A\sigma} - n_{Ai}) \rangle}{E - E_A - U \langle n_{A\bar{\sigma}} \rangle - \sum_k \frac{V_{Ak}^2}{E - E_k + \omega_{q\lambda}} + \omega_{q\lambda}} \right\} \dots (19) \end{aligned}$$

As done previously, Eq. (18) may be rewritten as:

$$G_{AA}(E) = \frac{1}{2\pi} \frac{E - T_A - U + F_{\bar{\sigma}} + U \langle n_{A\bar{\sigma}} \rangle}{(E - T_A - M_{q\lambda}^{ph})(E - T_A - U + F_{\bar{\sigma}}) - U F_{\bar{\sigma}}} \dots (20)$$

The roots of Eq. (20) may be obtained by solving the equation:

$$(E - T_A - M_{q\lambda}^{ph})(E - T_A - U + F_{\bar{\sigma}}) - U F_{\bar{\sigma}} = 0, \dots (21)$$

resulting in

$$\begin{aligned} E = T_A + \frac{1}{2} [(U - F_{\bar{\sigma}} + M_{q\lambda}^{ph}) \\ \pm \{(U + F_{\bar{\sigma}} + M_{q\lambda}^{ph})^2 + 4 F_{\bar{\sigma}} U\}^{1/2}] \dots (22) \end{aligned}$$

Within the approximation $(U + F_{\bar{\sigma}} + M_{q\lambda}^{ph}) \gg (F_{\bar{\sigma}} M_{q\lambda}^{ph})$, we get simplified roots of Eq. (21) as

$$\begin{aligned} E_1 = T_A + U + M_{q\lambda}^{ph} \\ E_2 = T_A - F_{\bar{\sigma}} \dots (23) \end{aligned}$$

The Green's function $G_{AA}(E)$ may be expressed as:

$$G_{AA}(E) = \frac{1}{2\pi} \left[\frac{1 - N_{q\lambda}^{ph}}{E - T_A + F_{\bar{\sigma}}} + \frac{N_{q\lambda}^{ph}}{E - T_A - U - M_{q\lambda}^{ph}} \right], \dots (24)$$

where

$$N_{q\lambda}^{ph} = \frac{\langle n_{A\bar{\sigma}} \rangle (F_{\bar{\sigma}} + M_{q\lambda}^{ph}) / U}{1 + (F_{\bar{\sigma}} + M_{q\lambda}^{ph}) / U} \dots (25)$$

This gives:

$$\begin{aligned} \rho_{AA}(E) = \frac{1}{\pi} \left[\frac{(1 - N_{q\lambda}^{ph}) \Delta(E)}{[E - E_A + F_{\bar{\sigma}} - \Lambda(E)]^2 + \Delta^2(E)} + \frac{N_{q\lambda}^{ph} (\Delta_1^{q\lambda}(E) + \Delta(E))}{[E - E_A + U - \Lambda(E) - \Lambda_1^{q\lambda}(E)]^2 + [\Delta_1^{q\lambda}(E) + \Delta(E)]^2} \right] \dots (26) \end{aligned}$$

where, we substitute

$$M_{q\lambda}^{ph} = \Lambda_1^{q\lambda}(E) - i \Delta_1^{q\lambda}(E) \dots (27)$$

Following as in the formalism of Anderson Hamiltonian, we find:

$$\langle n_{A\bar{\sigma}} \rangle = (1 - N_{q\lambda}^{ph}) F(E_A - F_{\bar{\sigma}} + \Lambda(E)) + N_{q\lambda}^{ph} F(E_A + U + \Lambda(E) + \Lambda_1^{q\lambda}(E)) \quad \dots (28)$$

This can be further simplified to obtain,

$$\langle n_{A\bar{\sigma}} \rangle = \frac{F(E_A - F_{\bar{\sigma}}) + (F_{\bar{\sigma}} + M_{q\lambda}^{ph}) / U F(E_A + U + \Lambda + \Lambda_1)}{1 + (F_{\bar{\sigma}} + M_{q\lambda}^{ph}) / U - F(E_A + U + \Lambda + \Lambda_1) + F(E_A - F_{\bar{\sigma}} + \Lambda)} \quad \dots (29)$$

In deriving the roots, we consider the approximation $(U + F_{\bar{\sigma}} + M_{q\lambda}^{ph}) \gg F_{\bar{\sigma}} M_{q\lambda}^{ph}$, which may also approximate Eq. (25) as $N_{q\lambda}^{ph} \ll \langle n_{A\bar{\sigma}} \rangle$. Therefore, Eq. (26) reduces to:

$$\rho_{AA}(E) = \frac{1}{\pi} \left[\frac{\Delta(E) (1 - \langle n_{A\bar{\sigma}} \rangle)}{[E - E_A + F_{\bar{\sigma}} - \Lambda(E)]^2 + \Delta^2(E)} + \frac{\langle n_{A\bar{\sigma}} \rangle [\Delta(E) + \Delta_1^{q\lambda}(E)]}{[E - E_A + U - \Lambda(E) - \Lambda_1^{q\lambda}(E)]^2 + [\Delta(E) + \Delta_1^{q\lambda}(E)]^2} \right] \quad \dots (30)$$

Case III – Occupation number can be simplified as follows:

$$\langle n_{A\bar{\sigma}} \rangle = \frac{F(E_a - F_{\bar{\sigma}} + \Lambda(E))}{1 - F(E_a + U + \Lambda + \Lambda_1) + F(E_a - F_{\bar{\sigma}} + \Lambda)} \quad \dots (31)$$

where generally the function F(x) is defined as²⁹⁻³⁵:

$$\frac{1}{\pi} \int_{-\infty}^{E_F} dE \rho(E) \left[(E - x - \Lambda(E))^2 + (\Delta^2 E) \right]^{-1} \quad \dots (32)$$

Thus, F(X) is function depending upon adatom energy and real part of self energy and $F_{\bar{\sigma}}$ where $F_{\bar{\sigma}} = E_2 - Ta + M_{\alpha\lambda}^h$ which depend on the strength of adatom-phonon interaction and this function modifies to density of state for adatom.

Case IV – Modified chemisorption energy

$$\Delta E = \int_{-\infty}^{E_F} \rho'(E) E dE - E_a - Un_{a30}^2 \quad \dots (33)$$

where $\rho'(E)$ modified density of states related adatom Green function; n_1 represents the average number of electron in the atom at the $|1\rangle$ state; E represents the variable energy on which various energy parameters depend on and E_F is the Fermi energy

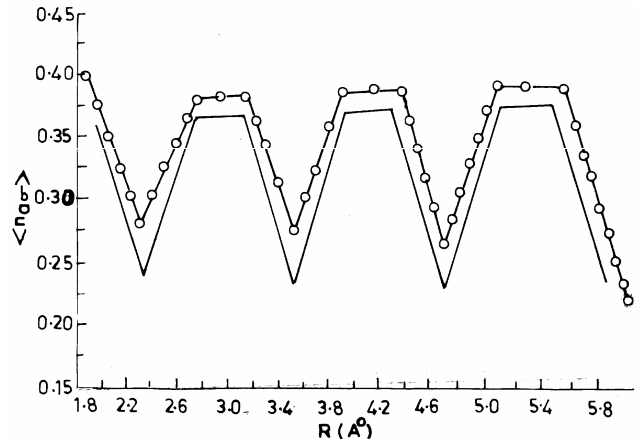


Fig. 1—Graph of occupation number $\langle n_{A\sigma} \rangle$ versus R of SWCNT (a) Solid line within the framework of Anderson's model; (b) —○— Line with inclusion of Adatom-phonon interaction to Anderson's model

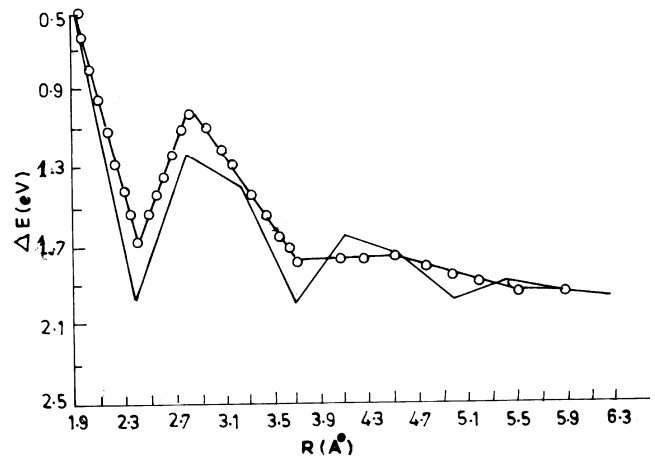


Fig. 2—Graph of ΔE versus R of SWCNT (c) Solid line represents within the framework of Anderson's model (d) —○— Line represents with inclusion of Adatom-phonon interaction to Anderson's model

5 Results and Discussion

Eqs. 31-33 reduce to that obtained by Anda *et al.*³⁶⁻³⁸ for $M_{q\lambda}=0$. It is, thus, observed that adatom-phonon interaction modifies the Adatom density of states and $\langle n_{A\sigma} \rangle$ which in turns modifies the chemisorption energy expression. From the above argument, it is clear that the function F(x) depends on the strength adatom-phonon interaction. It is also observed that the adatom phonon interaction shifts the energy of the bonding and antibonding states as described by Newns. In Fig. 1), when we calculate occupation number versus radius in Å of the SWCNT, the inclusion of adatom-phonon interaction modifies

in regular higher consistency manner and when we calculate the chemisorption energy versus radius in Å of single walled carbon nanotube and compare its with that only Anderson-Newns model it reveals regular reducing Zigzagness of the graph of chemisorption energy w.r.t. radius Å consistently Fig. 2). It is, therefore, interesting to calculate in detail from the 1st principle³⁹ the effect of adatom-phonon interaction on occupation number and chemisorption energy to reveal the surface properties of nanotubes along with other surface parameters like localization energy.

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