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Pressure effect on electrical conductivity of hydrogen molecular solid: Quantum mechanical approach

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Configuration Interaction method is used to calculate transfer integral of hydrogen molecular solid which is used to calculate its electrical conductivity. Using this new method we have calculated the transition pressure (2.8 Mbar) and critical density (1.302 gm/c^3) of hydrogen molecular solids which is found in very good agreement with the experimental results and other theoretical calculations.

Introduction

In present avenues of research there are widespread interests on molecular conductors [1] and superconductors [2]. Electrical conductivity of molecular solid is quite different from that of commonly used in solid state chemistry. Predictions of conducting molecular solids were made as early as 1911[3]. The first observation of high conductivity for a molecular compound, a perylene bromide salt, was reported by Akamatu et al [4]. In 1973 “organic metal” was characterized [5-6] and in 1980 first molecular super conductor [7] was reported by D. J érome et al.

Several structural and electronic criteria have been proposed for molecular conductors so far. In 1999 Kobayashi et al [8] in a seminal paper proposed a set of requirements for designing of single component natural molecular solids. The proposed requirements were a small HOMO-LUMO energy gap, large three dimensional transverse inter molecular interactions and probable formation of parallel bands. Here we have reported a new methodology to calculate the Direct Current (DC) conductivity of metals and molecular solids. In this approach, electron transfer is considered between two adjacent atoms (for metals) or molecules (for molecular conductors). Crystal structure is also important parameter for this calculation. Finally microscopic properties are related to bulk properties through conversion parameter (Ba) which takes care of all types of fluctuations due to change of system from microscopic level to macroscopic level.

This methodology is developed from the basic understanding of electrical conductivity using Drude model [9-10] which is of course a truly classical picture of electron gas. Quantum computational techniques are applied to obtain a relation between electrical conductivity and valance electron density in metallic or molecular crystals. Few known metals are used to evaluate the conversion parameter (Ba) involved for conductivity calculation at different temperatures. Finally pressure effect on electrical conductivity of solid molecular hydrogen [11] and that of diamond, graphite, pure silicon and doped silicon are tested which comes out with very good agreement of experimental results [12] and predictions from some other theories [13].

Theoretical Background

DC conductivity (σ) is ratio of current density (ĵ) to applied electrical potential (E). For DC potential current density (ĵ) would be given as

$$\hat{J} = -nev \qquad (1)$$

Here n is number of electrons per c.c., e is charge of electron and v is average velocity of electron due to the applied electric field. For unit potential, σ will be given as

$$\sigma = -nev \qquad (2)$$

In equation (2), ne is electronic charge density which is evaluated using quantum computational methods. In this work Configuration Interaction (CI) [14-15] techniques is used. It may consider that charge density is proportional to the electron probability density of valance electrons assuming that only valance electrons contribute to electrical conductivity. CI formalism is taken for quantum computation to include electron correlation effects. Though only electron density for valance electrons are considered core electrons contribution to electrical conductivity is also reflected through the formation of molecular wave function (MO). In an applied electrical field, electron transfer occurs from one atomic or molecular site to another. Using quantum chemical methodology we can verify whether electron transfer from one site to another site is possible or not. For good conductors it is expected that electron transfer must be quantum mechanically allowed and transfer integral would be large. DC conductivity should be proportional to the square of the transfer integral. In equation (2) we may replace electronic velocity (v) by √KE where KE is kinetic energy of electrons in the valance orbital. This approach is semi classical but very useful for theoretical calculations for electrical properties of conducting molecular solids. Thus DC conductivity may be defined in terms of charge density and kinetic energy as follows

$$\sigma = B_a \times \rho_e \times \sqrt{KE} \quad (3)$$

ρ_e is charge density of valance electron and B_a is proportionality constant. As stated above, B_a is in fact conversion parameter which is only constant for all conductors at a fixed temperature and bulk size that means whether it is in atomic scale size, nano scale size or in macroscopic scale size. All sorts of fluctuations due to phonon-phonon interactions, thermal disorderness and crystal defects etc. at macroscopic state are hidden in Ba. Thus change of temperature, crystal purity level or size of conductor (nano size or meso size) will affect B_a value. Valence electron density and transfer probability are calculated only for 0K but conductivity at high temperature is calculated using B_a value at that respective temperature as temperature effect reflects through Ba this is the beauty of this method. It is obvious that a positive value of KE implies electron transfer is quantum mechanically allowed and 0 or negative value means the respective process is forbidden.

Computational Details

GAMESS 16 (Version = 6 SEP 2001 (R5) from Iowa State University) is used for calculation of KE and ρ_e. STO-3G basis set is used for all calculations. Using GAMESS, we have calculated energy and CI coefficients for first 10 states for a pair of metal atoms (or molecules for molecular solids). ρ_e is calculated from overlap matrix and density matrix. Inclusion of higher states may improve the order of correctness of this calculation but for qualitative analysis this is sufficient for small systems. KE is calculated from overlap between different CI states. Finally conductivity is calculated from equation (3).

Result and Discussion

First, we have presented the calculated value of Ba for Li, Na, K, Be, Mg, Ca and

Al at 273K using known value of resistance (conductance). Temperature dependence of Ba is presented next. Using average value of Ba conductivity of molecular hydrogen is calculated for different H_2-H_2 distance and presented in Table-2. Transition pressure of hydrogen molecular solid from non-conducting phase to conducting phase is calculated from this study. We also have presented few tests for conductivity of doped species.

Determination of conversion parameter (B_a)

Some common metals are used for evaluation of B_a using known values of resistance from equation (3). Crystal distances and resistivity of metals are taken from reference [17] and [18]. In Table-1a B_a values for different metals at 273K are given. B_a varies from 1.5 to 2.03. Average value of B_a is 1.7×10^{10} mho gm$^{-1/2}$cmS in c.g.s. unit.

Table-1a: Conversion parameter (B_a) for different metals at 273K (in c.g.s. units)

Metal	Crystal type	Lattice spacing ($a\times10^8$)	Kinetic energy ($erg\times10^{12}$)	Probability density	Resistivity at 273K ($\rho\times10^6$)	Conversion parameter ($Ba\times10^{10}$)
Li	bcc	3.49	1.85	5.82	8.55	1.50
Na	bcc	4.23	195.32	1.02	4.20	1.68
K	bcc	5.23	25.76	2.06	6.10	1.57
Be	hcp	2.29	38.46	3.06	2.80	1.88
Mg	hcp	3.21	82.61	1.66	3.90	1.70
Ca	fcc	5.58	207.15	1.00	3.43	2.03
Al	fcc	4.05	269.82	1.62	2.45	1.53

In Table-1b B_a values for different metals at different temperature is shown. Due to lack of information about resistivity of few metals at some respective temperature B_a values were not calculated. From Table-1b it is found that B_a linearly increases with lowering of temperature but at very low temperature variation of B_a may be different. It is also found that at low temperature percentage variation of B_a for different metals is high where as at high temperature it is small. For a particular metal, variation of B_a at different temperature is smooth. Figure-1 describes temperature effect on B_a.

Table-1b: Conversion parameter (B_a) for different metals at different temperatures

Metal	Resistivity at 77K	B_a at 77K	Resistivity at 273K	B_a at 273K	Resistivity at 298K	B_a at 298K	Resistivity at 373K	B_a at 373 K
Li	1.04	12.17	8.55	1.50	9.32	1.36	12.4	1.02
Na	0.8	8.8	4.20	1.68	4.75	1.47	….	….
K	1.38	6.93	6.10	1.57	7.19	1.33	….	….
Be	….	….	2.80	1.88	3.25	1.62	5.3	0.99
Mg	0.62	10.71	3.90	1.70	4.3	1.55	5.6	1.19
Ca	….	….	3.43	2.03	3.6	1.94	5.0	1.39
Al	0.3	12.52	2.45	1.53	2.65	1.41	3.55	1.06
average	….	10.22	….	1.7	….	1.53	….	1.13

Variation of conversion parameter (B_a) with temperature. B_a values of Mg and Li are plotted against temperature. Also average values of B_a at different temperatures are plotted. Trend of variation is same for these three.

Study of hydrogen molecular solid

Following the work done by D. E. Ramakar, L. Kumar and F. E. Harris [19] DC conductivity of hydrogen molecular solid for different H_2-H_2 distances are calculated using equation (3) considering the solid separately as simple cubic structure and body centered cubic (bcc) structure at 273K. Results are shown in Table-2. At 1.726Å of H_2-H_2 bond distance, kinetic energy (KE) becomes negative which may be considered as the transition point of molecular hydrogen to metallic hydrogen. Conductance of metallic hydrogen considering bcc structure in metallic phase is 2.8 times higher than that for simple cubic structure. Near transition pressure, 2.8 Mbar, calculated density of hydrogen is 0.651 gm/c^3 for simple cubic crystal and 1.302 gm/c^3 for bcc. Experimental results reported by Grigor'ev et al [20] shows that at transition point density of hydrogen is in between 1.08 to 1.30 gm/c^3 which are comparable to the results obtained here for bcc crystal structure.

Table-2: Variation of kinetic energy and conductivity of hydrogen molecular solid at different pressure i.e. for different H_2-H_2 bond distances at 273K for B_a =1.76×10^{10} c.g.s unit (in c.g.s unit)

H_2-H_2 bond distance ×10^8	Kinetic energy (erg×10^{12})	Probability density	Conductance (σ ×10^{-5}) for simple cube	Conductance (σ ×10^{-5}) for Bcc
1.22	60.9	2.235	0.987	3.08
1.32	57.8	1.896	0.816	2.54
1.42	67.1	1.578	0.731	2.30
1.52	60.1	1.324	0.581	1.82
1.62	41.0	1.102	0.399	1.28
1.72	58.7	0.916	0.397	1.24
1.725	58.66	0.906	0.393	1.22
1.726	-23.7	….	….	….
1.727	-21.6	….	….	….
1.82	-27.6	….	….	….
1.92	-34.0	….	….	….

Variation of Kinetic energy of hydrogen molecular solid for different H_2-H_2 bond length

Kinetic energy of transferred electrons is plotted against H_2-H_2 bond length. There is a sudden fall at 1.725 Å which is the transition point.

Study of carbon and silicon

Kinetic energies are calculated for diamond, graphite, pure silicon and doped silicon. Results are shown in Table-3. KE is negative for diamond which is true for an insulator. For graphite situation is interesting. In case of intra layer C-C bond (1.42Å) KE is negative indicating non-conducting behavior but for inter layer C-C bond (3.35Å) KE is positive which justify the electrical conductivity of graphite through inter layer C-C bond which is again known to us. Due to presence of two different types of C-C bond graphite is anisotropic with respect to electrical conductivity which is also experimentally verified. For pure silicon KE is negative which becomes positive when it is doped with Phosphorus (P) or Boron (B) and becomes conductive but conductivity should depend on the percentage of doping. Results are presented in Table-3.

Table-3: Kinetic energy of transferred electron for diamond, graphite, silicon and doped silicon (in c.g.s unit)

Element	Lattice spacing ($a\times10^8$)	Kinetic energy ($erg\times10^{12}$)	Possibility of DC conductivity
Diamond	1.54	-52.2	Forbidden
Graphite(for intra plane C-C bond)	1.42	-88.2	forbidden
Graphite (for inter plane C-C bond)	3.35	52.0	allowed
Pure Silicon	2.73	-147.9	Forbidden
Silicon doped with Nitrogen	2.21	-40.1	forbidden
Silicon doped with Boron	2.62	1253.4	allowed

Silicon doped with Phosphorus	2.72	4186.6	allowed

Variation of DC conductivity of hydrogen molecular solid with H_2-H_2 bond length

Electrical conductivity of hydrogen molecular solid is plotted against H_2-H_2 bond length for two different geometries (sc and bcc). Conductivity for bcc is higher than that for sc.

Conclusion

From theoretical studies on hydrogen molecular solid, diamond, graphite, silicon and doped silicon it may be conclude that the theory for electrical conductivity described here is applicable for a wide range of metals and molecular solids for both qualitative and quantitative aspects. The art of this theory is lying under the opportunity of calculation of conductivity at any temperature knowing only valence electron density and transition probability at 0K and variation of B_a with temperature. Calculation of conductivity explicitly depends on conversion parameter B_a. Only temperature dependence of B_a is examined here, one can examine size dependence and dependence of B_a on crystal impurities and disorderliness. This theory is directly related to the pressure effect on DC conductivity and useful for calculation of transition pressure and density for molecular conductors.

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