Theoretical Study Of The Dependence Of Excitation Energy On Electron Density Profile And Strain In Metals

G.E. Adesakin *+ and O. F Famutimi*

* Department of Physics
Ekiti State University, Ado-Ekiti, Nigeria
+E-mail of corresponding author: adesakingbenga@gmail.com

Abstract: A model for the calculation of excitation energies of electron in metal is presented. The absolute value of the ratio between the lateral strain (shrinkage) and the longitudinal strain (elongation) is taking into consideration during computation. The result obtain revealed that excitation energy of metals decreases as electron density parameter r_s increases. This revealed that excitation energy of metals depend on bond length and number of carrier atom per unit volume. There is a good agreement between the computed and the ab-initio value of the excitation energy. Excitation energy of metals reduces as strain rises, this shows that as strain rises the ductility, intra-band electron transition probabilities and stiffness of metals decreases which there by forces the excitation energy of metals to reduce as strain rises. The result obtained for excitation energy of electron in metals in this work is novel and very promising for a broad range of future applications.

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Introduction

Metals are metallic elements (e.g., iron, aluminum, copper, titanium, gold, nickel), and nonmetallic elements (e.g., carbon, nitrogen, oxygen) (Kakani and Kakani, 2004). Atoms in metals and their alloys are arranged in a very orderly manner and are relatively dense in comparison to ceramics and polymers. With regard to mechanical characteristics, metals are relatively stiff and strong, ductile (i.e., capable of large amounts of deformation without fracture), and resistant to fracture. This accounts for their widespread use in structural applications (Pillai, 2010). Metallic materials have large numbers of non-localized electrons (Animalu, 1977). Many properties of metals are directly attributable to electrons. For example, metals are extremely good conductors of electricity. Excitation is the transfer of electron from ground state atom to higher energy level when energy is added to the system. These extra energy is called excitation energy (Ashcroft and Mermin, 1977). Excitation energy is the energy require to remove an electron from an atom or molecule. Excitation energy is the difference between the ground state and the first excited state (Kakani and Kakani, 2004). Excitation energy of a system is often determined experimentally via spectroscopy. The concept of excitation energy is important in the fields of chemistry, physics and engineering. In chemistry, excitation energy is used to determine the energetics of chemical reactions. In physics, excitation energy is used to describe the behaviour of particles in an excited state while excitation energy is used to design and optimize energy systems in engineering (Kakani and Kakani, 2004). The potential difference through which an electron is accelerated to acquire the value of excitation energy is called excitation potential (Animalu, 1977). The concept of mean excitation energy is the ability of a medium to absorb energy from any kind of incident radiation (either photons or charged particles) (Efthimios, 2003). Excitation can be refer to as the addition of a defined amount of energy (called excitation energy) to a system such as atomic nucleus, atom, or molecule (Kittel, 1976). Mechanical properties of a material, such as strength, describe how a material withstands applied forces, including tensile or compressive forces, impact forces, cyclical or fatigue forces, or forces at high temperatures Kiejna and Pogosov (1999). During elastic deformation, atoms in solid are slightly and temporarily displaced from their equilibrium positions (Kakani and Kakani, 2004). When an applied stress that has induced elastic elongation is removed in solid the deformation is reversed and the recovery to the original shape occurs almost instantly except in viscoelastic polymers (Kittel, 1976). The free-electron model provides a fair account of the outermost electrons in metal or semiconductor (Kachhava, 1992). A better understanding of the magnetism of electrons in solids is achieved by considering the situation for free atoms (Pillai, 2010). Electron emission from a material surface occurs through three main possible processes; photoemission, thermionic emission, and field emission. Photoemission occurs when an electron absorbs photonic energy allowing the electron to emit above the vacuum level Busch and Schade (1976). Thermionic emission is a process where thermal energy causes a broadening of the electron distribution such that some higher energy electrons will emit into vacuum. (Ashcroft and Mermin, 1977) Field emission is a quantum mechanical process in which electrons are able to tunnel through the surface barrier under high electric fields (Rogalski and Palmer, 2000). Over the course of the last century, many advances have occurred in the study of excitation energy of electron in different material. Khmelinskii et. al (2019) presented a report on excited state (exaction) propagation in a metal nanotrack over macroscopic distances and the energy transfer from the nano-track to adsorbed dye molecules. They concluded that the effective speed of exciton propagation along the nano-track is much lower than the surface plasmon propagation speed and the energy transfer between the nanotrack. The adsorbed dye is limited by excited-state lifetime in the nanotrack. Also, the measured characteristic buildup time of the dye emission is much longer than the characteristic energy transfer time to the dye. Früchtl et. al (2022) use density functional theory (DFT) calculations to show that combination of electric field and electronic excitation is a promising mechanism to force a molecular switch based on amino-imino tautomerisation into one of its two states. By calculating the effect of an electric field in the direction of the moving hydrogen on the shape of the barrier in the ground and low-lying excited states of previously proposed molecular switches consisting of some membered rings with adjacent amino and imino groups, they demonstrate that electric fields and photons in experimentally accessible ranges introduce sufficient asymmetry to push the switch into the desired configuration. Excitation to states with inverted order of the preferred geometry allows reversible switching without reversal of the electric field. John R. Sabin and Jens Oddershede (1989) compute the atomic dependent stopping power of some metallic targets using the kinetic theory of stopping. He obtained electron velocity distributions from measured solid-state Compton profiles and the mean excitation energies by matching the calculated stopping curves to experimental data in the projectile energy range. This results yield stopping curves which agree quantitatively with experimental measurements in the projectile energy region. They also demonstrate that the decomposition of the mean excitation energy into orbital contributions is important for determination of the stopping cross section and then conclude that assigning different orbital mean excitation energies to different shells leads to large modifications of the commonly accepted total mean excitation energy. Kovacs (2006) employed a hyperthermal hydrogen/deuterium atom beam source with a defined energy distribution to investigate the kinetically induced electron emission from noble metal surfaces. A monotonous increase in the emission yield was found for energies along with an observed isotope effect described in terms of model based on Boltzmann type electron energy distributions. Quijada et. al (2006) studied the lifetime of electronic excitations in metal nanoparticles using time dependent density functional theory. The result obtained revealed that electronic excitations in metal particles with sizes up to a few nanometers are shown to have a one-electron character when a laser pulse is applied off the plasmon resonance. The calculated lifetimes of these excitations are in the femtosecond timescale but their values are substantially different from those in bulk. This deviation can be explained from the large weight of the excitation wave function in the nanoparticle surface region, where dynamic screening is significantly reduced. The well-known quadratic dependence of the lifetime with the excitation energy in bulk breaks down in these finite-size systems. In this work, electron approximation theory is extended to the study of excitation energy of electron in metals and its dependence on linear strain is investigated.

Theoretical Considerations

The total energy of solid for configuration of ions is given by

$$E^{tot} = T + U^{ion-el} + U^{el-el} + U^{ion-ion} \qquad (1)$$

Where T is the kinetic energy of electron, U^{ion-el} is the energy due to ion-electron attractive interaction, U^{el-el} is energy due to electron-electron interaction including the Coulomb repulsion and exchange and correlation effects and $U^{ion-ion}$ is energy due to ion-ion repulsive interaction. The last term in equation (1) is the Madelung energy.

$$U^{ion-el} = \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J e^2}{|R_I R_J|} \qquad (2)$$

with Z_I as the valence charge of ion at position Z_J which can be calculated by Ewald method

$$U^{ion-ion} = \frac{1}{2}\sum_J Q_J \phi(R_J) = \frac{2\pi}{\Omega}\sum_{I,J}\sum_{G=0} Q_I Q_J \frac{e^{iG(R_I-R_J)}}{|G|^2} \qquad (3)$$

where G is reciprocal space vectors, Ω is the volume of the crystal, Q_I and Q_J is point charges located at R_I and R_J. The term $\phi(r)$ is

$$\phi(r) = 4\pi \sum_G \rho(G) e^{iG.r} \frac{1}{|G|^2} \qquad (4)$$

The expression in equation (4) gives the charge density as

$$\rho(r) = \sum_I Q_I \delta(r - R_I) \rightarrow \rho(G) = \frac{1}{\Omega} \sum_I Q_I \, e^{iG.R_I} \qquad (5)$$

while the total potential takes the form

$$\phi(r) = \frac{4\pi}{\Omega} \sum_I \sum_{G \neq 0} Q_I \frac{e^{iG(r-R_I)}}{|G|^2} \qquad (6)$$

Where the term G=0 excluded from the summation is consistent with the average charge and potential that both vanish. Using the single particle approximation, other terms in equation (1), $E^{XC}[n(r)]$ take the form

$$T = \sum_k \left\langle \Psi_k \middle| -\frac{\hbar^2 \nabla_r^2}{2m_e} \middle| \Psi_k \right\rangle \qquad (7)$$

$$U^{ion-el} = \sum_k \langle \Psi_k | V^{ps}(r) | \Psi_k \rangle \qquad (8)$$

$$U^{el-el} = \frac{1}{2} \sum_{kk'} \left\langle \Psi_k \Psi_{k'} \middle| -\frac{e^2}{|r-r'|} \middle| \Psi_k \Psi_{k'} \right\rangle + E^{XC}[n(r)] \qquad (9)$$

Where $|\Psi_k\rangle$ are the single particle states obtained from a self-consistent solution of the set of single-particle Schrodinger equations and $n(r)$ is the electron density. For simplicity, single index k is use to identify single particle wave functions with the understanding that it encompasses both the wave vector and the band index. In terms of these states, the density is given by

$$n(r) = \sum_{k(\varepsilon_k < \varepsilon_f)} |\Psi_k(r)|^2 \qquad (10)$$

with the summation running over all occupied states with energy ε_k below the Fermi level ε_f. $V^{ps}(r)$ is the external potential that each valence electron in the solid experiences due to the presence of ions described by pseudopotentials and is the exchange and correlation contribution to the total energy in the framework of density functional theory depends on the electron density. By adopting local density approximation for exchange correlation function in terms of electron density

$$E^{XC}[n(r)] = \int \varepsilon^{XC}[n(r)] n(r) dr \qquad (11)$$

with $\varepsilon^{XC}[n(r)]$ being the local function of the density that accounts for exchange and correlation effects. The potential due to exchange and correlation effects that appears in the single-particle equations

$$V^{XC}(r) = \frac{\partial}{\partial n(r)} [\varepsilon^{XC}[n(r)] n(r)] = \varepsilon^{XC}[n(r)] + \frac{\partial \varepsilon^{XC}[n(r)]}{\partial n(r)} n(r) \qquad (12)$$

And the single-particle equations take the form

$$\left[-\frac{\hbar^2 \nabla_r^2}{2m_e} + V^{ps}(r) + \int \frac{e^2 n(r')}{|r-r'|} dr' + V^{XC}(r) \right] |\Psi_k\rangle = \varepsilon_k |\Psi_k\rangle \qquad (13)$$

Multiplying equation (13) by $\langle \Psi_k|$ from the left and summing over all occupied states, we obtain

$$\sum_{k(\varepsilon_k < \varepsilon_f)} \left[\left\langle \Psi_k \middle| -\frac{\hbar^2 \nabla_r^2}{2m_e} \middle| \Psi_k \right\rangle + \langle \Psi_k | V^{ps}(r) | \Psi_k \rangle \right] + \iint \frac{e^2 n(r) n(r')}{|r-r'|} \mathrm{d}r dr' + \int V^{XC}(r) n(r) dr = \sum_{k(\varepsilon_k < \varepsilon_f)} \varepsilon_k \qquad (14)$$

Comparing equation (14) with equation (1) for the total energy using equation (9)

$$E^{tot} = \sum_{k(\varepsilon_k < \varepsilon_f)} \varepsilon_k - \frac{1}{2} \int V^{Coul}(r) n(r) dr - \int \nabla V^{XC}(r) n(r) dr + U^{ion-ion} \qquad (15)$$

where the Coulomb potential is

$$V^{Coul}(r) = \int \frac{e^2 n(r')}{|r-r'|} \, dr' \qquad (16)$$

and the difference in exchange and correlation potential is

$$\Delta V^{XC}(r) = V^{XC}(r) - \varepsilon^{XC}[n(r)] \qquad (17)$$

when accounting for the infinite terms, we compensate for the alteration introduced by the pseudopotential. This is done by adding the term ΔU^{ps} to the total energy. Hence

$$\Delta U^{ps} = \sum_I Z_I \int \left[V_I^{ps}(r) + \frac{Z_I e^2}{r} \right] dr \qquad (18)$$

The total energy of solid takes the form

$$E^{tot} = \sum_{k(\varepsilon_k < \varepsilon_f)} \varepsilon_k - 2\pi e^2 \Omega \sum_{G \neq 0} \frac{[n(G)]^2}{|G|^2} - \Omega \sum_G \Delta V^{XC}(G) n(G) + \Delta U^{ps} + U^{ion-ion} \qquad (19)$$

Using free electron theory, the excitation energy E_x of electron in metals is obtain as

$$E_x = E_k + \phi + E_B = \frac{3}{5} \left[\frac{50.1}{r_s^2} \right] + \frac{43.46}{{r_s}^{3/2} {E_F}^{1/2}} + \frac{9e_0^2}{10} \left[\frac{2.45a_0}{2r_s^2} - \frac{1}{r_s} \right] \qquad (20)$$

Where E_k is the average kinetic energy, ϕ is the work function, E_B is the binding energy, E_F is the Fermi energy, r_s is electron density parameter, a_0 is Bohr radius, $e_0 = {e}/{\sqrt{4\pi\varepsilon_0}}$, e is electronic charge and ε_0 is permittivity of free space.

In this work, excitation energy of electron in metals is computed using equation (20).the metals were chosen base on their industrial and technological applications.

Results and Discussion

Figure 1 shows the plot of excitation energy against electron density parameter for alkali, earth alkali, group three, noble and transition metals. Figure show that excitation energy of metals decreases as electron density parameter r_s increases with metals in the region of high density limit having high excitation energy than metals in the region of low density limit. This revealed that excitation energy of metals depend on bond length and number of carrier atom per unit volume. The trend display by metals in figure 1 also revealed that excitation energy of electron in metals relied on the number of valence electron per unit cell in metals. The result obtained in figure 1 shows that there is a good agreement between the computed and the ab-initio value of the excitation energy. This indicates that free electron theory used in this work is useful in the theoretical predictions of some properties of metals. The ab-initio value is obtained by inserting the experimental value of Fermi energy obtained from solid state Physics by Ashcroft and Mermin (1976) into the model used for computation. The high and low value of excitation energy posses by metals in the region of high and low density limit may be due to the nature of principal and angular momentum quantum number posses by metals in this region of density limit. The high value of excitation energy posses by metals in the region of high density limit in figure 1 may also be due to the high electron principal quantum number that are farther away from the nucleus posses by metals in this region of density limit. Figure 2 shows a plot of excitation energy as ordinate with strain as abscissa for metals. The result obtained revealed that excitation energy of metals reduces as strain rises, this shows that as strain rises the ductility, intra-band electron transition probabilities and stiffness of metals decreases which there by forces the excitation energy of metals to reduce as strain rises. Figure 2 also revealed that, when strain is high excitation energy of electron in metal is low and when strain is low excitation energy of electron in metals is high. This suggest that there is deviations in standard atomic distance between electrons in the metals. Another thing that may be responsible for the decrease in excitation energy as strain rises in figure 2 could be due to the alterations in band gap, electronic structure, electron density of state and delocalization of electrons energy level alignment in the metals.

Conclusion

This review has provided an overview of excitation energy of electron in metals dependence on electronic density profile and strain. The high and low value of excitation energy posses by metals in the region of high and low density limit may be due to the nature of principal and angular momentum quantum number posses by metals in this region of density limit. The high value of excitation energy posses by metals in the region of high density limit may also be due to the high electron principal quantum number that are farther away from the nucleus posses by metals in this region of density limit. The decrease in excitation energy as strain increases could be due to the alterations in band gap, electronic structure, electron density of state and delocalization of electrons energy level alignment in the metals.

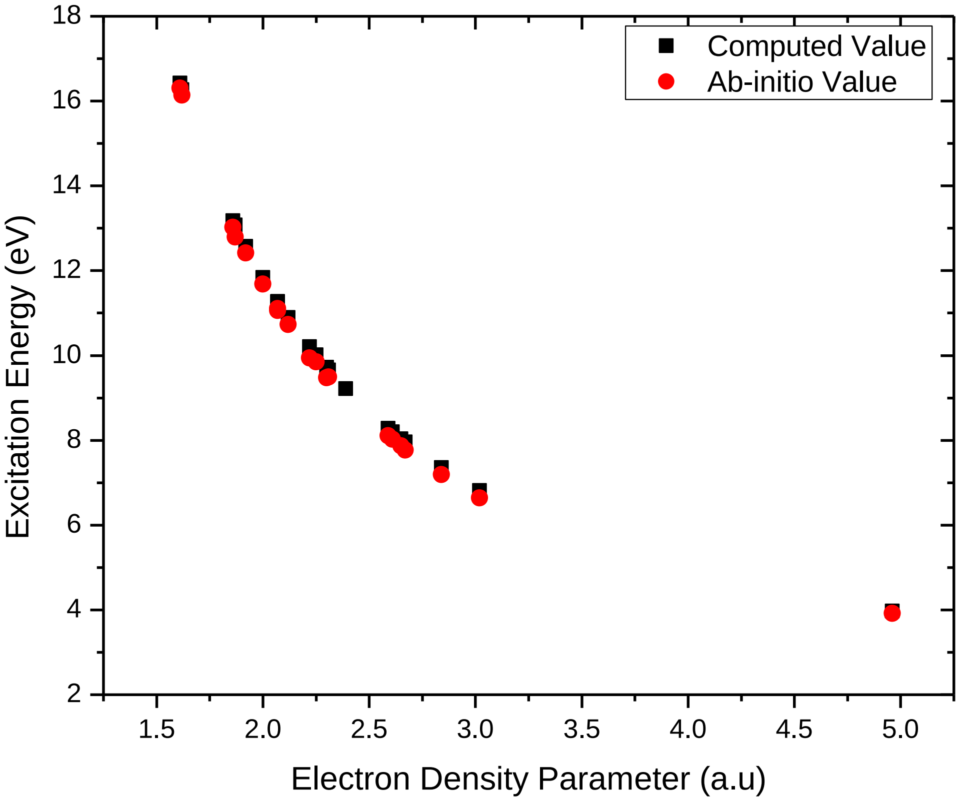
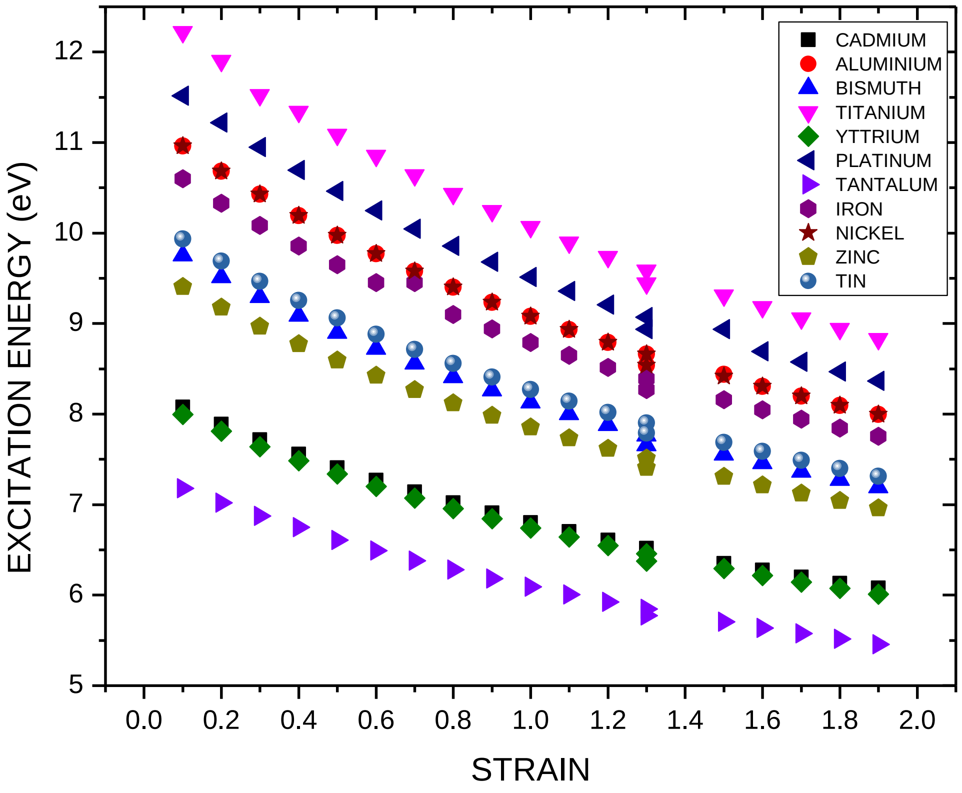


Figure 1: Plot of Excitation Energy as ordinate with Electron Density Parameter as abscissa for Metals


EXCITATION ENERGY (eV)
STRAIN
5
6
7
8
9
10
11
12
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
CADMIUM
ALUMINIUM
BISMUTH
TITANIUM
YTTRIUM
PLATINUM
TANTALUM
IRON
NICKEL
ZINC
TIN

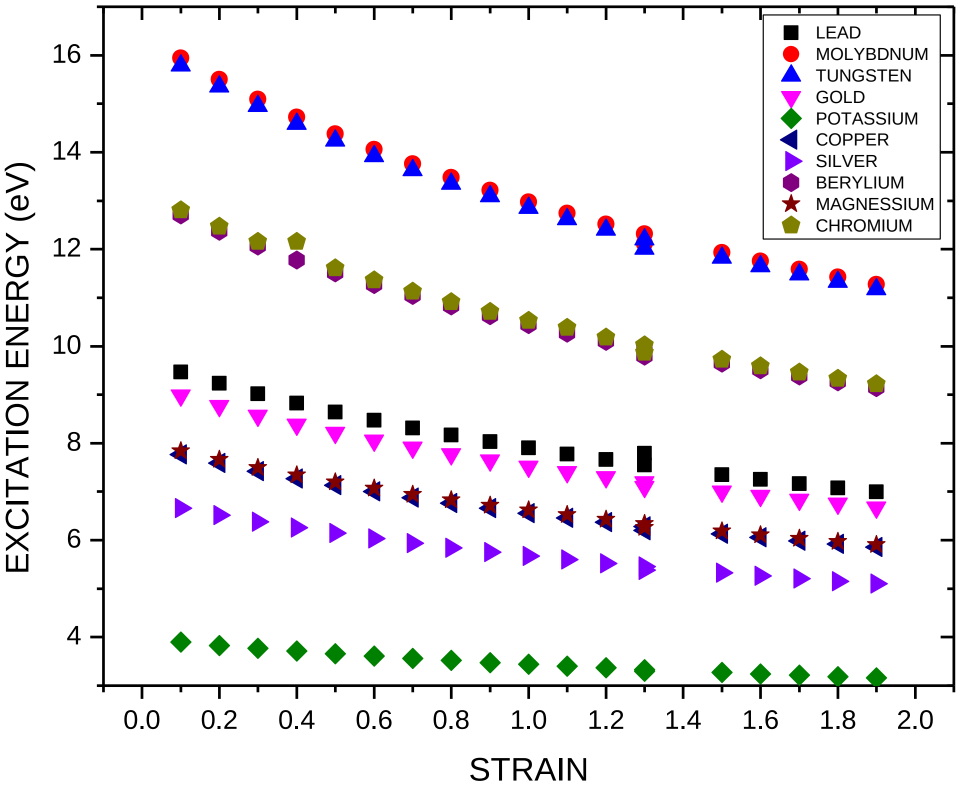


Figure 2: Plot of Excitation Energy as ordinate with Strain as abscissa for Metals

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Table 1: Excitation Energy of Metals

Metals	**Electron Density Parameter r_s (a.u)**	**Computed Excitation Energy (eV)**	**Ab-initio Excitation Energy (eV)**
K	4.96	3.96796	3.91833
Cu	2.67	7.95976	7.77156
Ag	3.02	6.81501	6.64201
Be	1.87	13.0730	12.7923
Mg	2.65	8.03779	7.86662
Cr	1.86	13.1778	13.0248
Fe	2.12	10.8911	10.7280

Ni	2.07	11.2688	11.1039
Zn	2.31	9.65861	9.49097
Cd	2.59	8.28181	8.10701
Al	2.07	11.2688	11.0622
Bi	2.25	10.0166	9.85152
Ti	1.92	12.5720	12.4155
Y	2.61	8.19876	8.02702
Sn	2.22	10.2058	9.94314
Pb	2.30	9.71649	9.47679
Mo	1.61	16.4252	16.3035
W	1.62	16.2673	16.1426
Au	2.39	9.21957	6.66468
Pt	2.00	11.8428	11.6857
Ta	2.84	7.35604	7.18901

Table 2: Excitation Energy of Strained Metals

		Strain								
Metals	**Strain**	**0.2**	**0.4**	**0.6**	**0.8**	**1.0**	**1.2**	**1.4**	**1.6**	**1.8**
K	4.96	3.82910	3.71062	3.60789	3.51764	3.43748	3.36563	3.30070	3.24162	3.18754
Cu	2.67	7.58638	7.27086	6.99972	6.76352	6.55536	6.37011	6.20386	6.05360	5.91688
Ag	3.02	6.51221	6.25593	6.03537	5.84297	5.67319	5.52190	5.38597	5.26296	5.15095
Be	1.87	12.3699	11.7780	11.2711	10.8309	10.4442	10.1010	9.79384	9.51693	9.26566
Mg	2.65	7.65953	7.33992	7.06530	6.82607	6.61526	6.42768	6.25934	6.10719	5.96878
Cr	1.86	12.4678	12.1568	11.3583	10.9138	10.5233	10.1768	9.86673	9.58719	9.33353
Fe	2.12	10.3307	9.85851	9.45365	9.10176	8.79223	8.51759	8.27117	8.04900	7.84725
Ni	2.07	10.6840	10.1915	9.76876	9.40167	9.07888	8.79227	8.53556	8.30399	8.09373
Zn	2.31	9.17772	8.77209	8.42405	8.12127	7.85483	7.61798	7.40739	7.21406	7.03990
Cd	2.59	7.88824	7.55582	7.27028	7.02158	6.80248	6.60755	6.43267	6.27462	6.13086
Al	2.07	10.6840	10.1912	9.76876	9.40167	9.07888	8.79227	8.53556	8.30399	8.09373
Bi	2.25	9.51280	9.08786	8.72343	8.40644	8.12751	7.87969	7.65761	7.45712	7.27500
Ti	1.92	11.9019	11.3376	10.8543	10.4345	10.0656	9.73819	9.44512	9.18084	8.94098
Y	2.61	7.81041	7.48236	7.20053	6.95507	6.73878	6.54636	6.37371	6.21768	6.07575
Sn	2.22	9.68978	9.25467	8.88150	8.55698	8.27150	8.01782	7.79054	7.58537	7.39901
Pb	2.30	9.23188	8.82317	8.47247	8.16738	7.89890	7.66031	7.79054	7.25339	7.07796
Mo	1.61	15.4990	14.7201	14.0539	13.4758	12.9686	12.5188	12.1167	11.7545	11.4259
W	1.62	15.3517	14.5817	13.9230	13.3516	12.8500	12.4053	12.0077	11.6495	11.3246
Au	2.39	8.76675	8.38455	8.05660	7.77115	7.51987	7.29649	7.09624	6.91535	6.75095
Pt	2.00	11.2205	10.6963	10.2472	9.85689	9.51386	9.20932	8.93665	8.69070	8.46741
Ta	2.84	7.02010	6.74951	6.49171	6.27872	6.09092	5.92366	5.77350	5.63768	5.51406

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