

Introduction to density functional theory

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I. INTRODUCTION

Density functional theory is a variational method that is presently the most successful approach to compute the electronic structure of matter. Its applicability ranges from atoms, molecules and solids to nuclei and quantum and Classical fluids. The density functional theory is derived from the N -particle *Schrödinger* equation and is entirely expressed in terms of the density distribution of the ground state $\rho_{GS}(\mathbf{r})$ and the single particle wave function ϕ_j . DFT reduces the calculations of the ground state properties of systems of interacting particles exactly to the solution of single-particle Hartree-type equations. This is why it has been most useful for systems of very many electrons. In this review we are going to discuss briefly the formulation of DFT.

II. THOMAS-FERMI THEORY FOR ELECTRON DENSITY

The Thomas-Fermi theory says for interacting electrons moving in an external potential $v(\mathbf{r})$, the relation between $v(\mathbf{r})$ and the density distribution $\rho(\mathbf{r})$ is:

$$\rho(\mathbf{r}) = \gamma(\mu - v_{eff}(\mathbf{r}))^{3/2} \quad (1)$$

$$v_{eff}(\mathbf{r}) \equiv v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2)$$

where $\gamma = \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2}$ and μ is the \mathbf{r} independent chemical potential and the second term in eq.(2) is the classical electrostatic potential generated by the density $\rho(\mathbf{r})$. Eq. 1 works best for systems of slowly varying density.(1),(2).

III. THE FIRST HOHENBERG-KOHN THEOREM

Hohenberg and Kohn started from Thomas-Fermi theory and establish the connection between the electron density and the many-electron *Schrödinger* equation (which is expressed in terms of $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$).

We start with Hohenberg-Kohn theorems which are at the heart of the density functional theory.

The first Hohenberg-Kohn theorem states that

The ground state density $\rho_{GS}(\mathbf{r})$ of a bound system of interacting electrons in some external potential $v(\mathbf{r})$ determines this potential uniquely (3),(4).

Proof: This proof is valid for a non-degenerate ground state. Let $\rho_{GS}(\mathbf{r})$ be a non-degenerate ground state density of N electrons in the potential $v_1(\mathbf{r})$ corresponding to the ground state ψ_1 and the energy E_1 . Then

$$E_1 = \langle \psi_1 | H_1 | \psi_1 \rangle = \int v_1(\mathbf{r}) \rho_{GS}(\mathbf{r}) d\mathbf{r} + \langle \psi_1 | T + V_{ee} | \psi_1 \rangle \quad (3)$$

where H_1 is the total Hamiltonian corresponding to v_1 , T and V_{ee} are the kinetic and interaction energy operators for the electrons. Let us now assume that there exists a second potential $v_2(\mathbf{r})$, not equal to $v_1(\mathbf{r}) + \text{constant}$, with

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ground state ψ_2 , necessarily $\psi_2 \neq e^{i\theta}\psi_1$ which gives rise to the same $\rho_{GS}(\mathbf{r})$. Thus

$$E_2 = \int v_2(\mathbf{r})\rho_{GS}(\mathbf{r})d\mathbf{r} + \langle\psi_2|T + V_{ee}|\psi_2\rangle \quad (4)$$

Since ψ is assumed to be non-degenerate, the Rayleigh-Ritz minimal principle gives

$$\begin{aligned} E_1 < \langle\psi_2|H_1|\psi_2\rangle &= \int v_1(\mathbf{r})\rho_{GS}(\mathbf{r})d\mathbf{r} + \langle\psi_2|T + V_{ee}|\psi_2\rangle \\ &= E_2 + \int (v_1(\mathbf{r}) - v_2(\mathbf{r}))\rho_{GS}(\mathbf{r})d\mathbf{r} \end{aligned} \quad (5)$$

$$\begin{aligned} E_2 < \langle\psi_1|H_2|\psi_1\rangle &= \int v_2(\mathbf{r})\rho_{GS}(\mathbf{r})d\mathbf{r} + \langle\psi_1|T + V_{ee}|\psi_1\rangle \\ &= E_1 + \int (v_2(\mathbf{r}) - v_1(\mathbf{r}))\rho_{GS}(\mathbf{r})d\mathbf{r} \end{aligned} \quad (6)$$

Addition of Eq. (5) and (6) leads to the contradiction

$$E_1 + E_2 < E_1 + E_2.$$

Therefore it is proved that the existence of a second potential which is not equal to $v_1(\mathbf{r}) + \text{constant}$ and gives the same $\rho_{GS}(\mathbf{r})$ must be wrong.

Also, $\rho_{GS}(\mathbf{r})$ determines the number of electrons, N

$$N = \int \rho_{GS}(\mathbf{r})d\mathbf{r} \quad (7)$$

Since $\rho_{GS}(\mathbf{r})$ determines both N and $v(\mathbf{r})$, it gives us the full H and all properties derivable from H through the solution of time independent or time dependent *Schrödinger* equation (even in the presence of the additional perturbation like electromagnetic fields). For example, the many body eigenstates $\psi^0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, $\psi^1(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \dots$, the 2 particle Green's function $G(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2)$ and so on. This theory is extended later in the case of degenerate ground state(5) and is also valid for the special case of non interacting electrons.

IV. THE SECOND HOHENBERG-KOHN THEOREM

The most important property of an electronic ground state is its energy E_{GS} . We can calculate it by variational principle:

$$E_{GS} = \min_{\psi} \langle\psi|H|\psi\rangle \quad (8)$$

Hohenberg and Kohn expressed the minimum energy using density. (I am using the derivation from R.O. Jones(8) (but Levy(6) and Lieb(7) first shown the derivation in this way which is simpler than the original derivation by Hohenberg and Kohn)). We consider N electrons moving in an external potential $v_{ext}(\mathbf{r})$, i.e., the hamiltonian is

$$H = T + V_{ee} + \sum_{i=1}^N v_{ext}(\mathbf{r}_i), \quad (9)$$

where H and V_{ee} are the kinetic and electron-electron interaction operators, respectively. Now Levy defined a universal functional (since the functional does not refer to any specific system and any specific potential)

$$F[\rho] = \min_{\psi \rightarrow \rho} \langle\psi|T + V_{ee}|\psi\rangle, \quad (10)$$

or

$$F[\rho] = \langle\psi_{min}^{\rho}|T + V_{ee}|\psi_{min}^{\rho}\rangle \quad (11)$$

where the minimum is taken over all ψ that give ρ . The density ρ at any position \mathbf{r}_1 is defined to be

$$\rho(\mathbf{r}_1) = N \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N \psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (12)$$

The second Hohenberg-Kohn theorem states

$$E[\rho] \equiv \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) + F[\rho] \geq E_{GS}, \quad (13)$$

and

$$\int d\mathbf{r} v_{ext}(\mathbf{r}) \rho_{GS}(\mathbf{r}) + F[\rho_{GS}] = E_{GS}. \quad (14)$$

Proof: Writing $v = \sum_{i=1}^N v_{ext}(\mathbf{r}_i)$ we get

$$\int d\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) + F[\rho] = \langle \psi_{min}^\rho | v + T + V_{ee} | \psi_{min}^\rho \rangle \geq E_{GS}, \quad (15)$$

according to the minimum property of the ground state. Using the minimum property once more we get

$$E_{GS} = \langle \psi_{GS} | v + T + V_{ee} | \psi_{GS} \rangle \leq \langle \psi_{min}^{\rho_{GS}} | v + T + V_{ee} | \psi_{min}^{\rho_{GS}} \rangle. \quad (16)$$

Now subtracting the interaction with the external potential we get

$$\langle \psi_{GS} | T + V_{ee} | \psi_{GS} \rangle \leq \langle \psi_{min}^{\rho_{GS}} | T + V_{ee} | \psi_{min}^{\rho_{GS}} \rangle. \quad (17)$$

The above equation is true only when

$$\langle \psi_{GS} | T + V_{ee} | \psi_{GS} \rangle = \langle \psi_{min}^{\rho_{GS}} | T + V_{ee} | \psi_{min}^{\rho_{GS}} \rangle. \quad (18)$$

Then we have

$$\begin{aligned} E_{GS} &= \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho_{GS}(\mathbf{r}) + \langle \psi_{GS} | T + V_{ee} | \psi_{GS} \rangle \\ &= \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho_{GS}(\mathbf{r}) + \langle \psi_{min}^{\rho_{GS}} | T + V_{ee} | \psi_{min}^{\rho_{GS}} \rangle \\ &= \int d\mathbf{r} v_{ext}(\mathbf{r}) \rho_{GS}(\mathbf{r}) + F[\rho_{GS}]. \end{aligned} \quad (19)$$

Hence the second Hohenberg-Kohn theorem is proved. It follows from eq.(18) that if the ground state is non-degenerate, $\psi_{min}^{\rho_{GS}} = \psi_{GS}$. If the ground state is degenerate $\psi_{min}^{\rho_{GS}}$ is equal to one of the ground state wave functions, and the others can also be obtained. The ground state density then determines the ground state wave function(s), from which all properties (including the ground state energy) can be calculated. These properties are therefore functionals of the density which the Hohenberg-Kohn theorem has stated before. But these theorems does not tell us the form of the functional dependence of energy on the density. Hohenberg and Kohn only states that to get back to the Thomas-Fermi theory, $\langle V_{ee} \rangle$ with respect to the ground state can be written as

$$\langle \psi_{GS} | V_{ee} | \psi_{GS} \rangle = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho_{GS}(\mathbf{r}) \rho_{GS}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (20)$$

but did not give the density representation of the kinetic energy part of the electrons. At this point Kohn-Sham gave a set of single particle equations which largely remedied the problem involving the form of kinetic energy and was the next major step in the development of DFT.

V. THE SELF-CONSISTENT KOHN-SHAM EQUATIONS

Kohn-sham self-consistent equations are very similar to the Hartree self-consistent single particle equations for the approximate description of the electronic structure of atoms (Hartree equations are based on Thomas-Fermi theory where every electron is regarded as moving in an effective single particle potential). Hartree equations are the following

$$\left\{ -\frac{1}{2}\nabla^2 + v_H(\mathbf{r}) \right\} \phi_j(\mathbf{r}) = E_j \phi_j(\mathbf{r}) \quad (21)$$

$$\rho(\mathbf{r}) = \sum_{j=1}^N |\phi_j(\mathbf{r})|^2 \quad (22)$$

$$v_H(\mathbf{r}) = -\frac{Z}{r} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (23)$$

where in eq.(21) j denotes both spatial and spin quantum numbers, $\rho(\mathbf{r})$ in eq.(22) is the mean density (for which, in the ground state, the sum runs over N lowest eigenvalues) and $v_H(\mathbf{r})$ in eq.(23) is the effective single particle potential. In the expression for $v_H(\mathbf{r})$ the first term represents the potential due to a nucleus of atomic number Z and the second term represents the potential due to the average density distribution $\rho(\mathbf{r})$.

In the way to solve these equations one may start from a first approximation (e.g., Thomas-Fermi theory), construct $v_H(\mathbf{r})$, solve eq.(21) and recalculate $\rho(\mathbf{r})$ from eq.(22), which should be the same as the initial $\rho(\mathbf{r})$. If it is not one iterates appropriately until it is.

The Hartree differential equation(21) takes the form of the *Schrödinger* equation for non-interacting electrons moving in the external potential v_{eff} . So for such a system the HK variational principle becomes

$$E_{v(\mathbf{r})}[\rho] \equiv \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) + T[\rho(\mathbf{r})] \geq E_{GS}, \quad (24)$$

where $T[\rho(\mathbf{r})]$ is the kinetic energy of the ground state of non-interacting electrons with density distribution $\rho(\mathbf{r})$. We want eq(22) to be stationary with respect to the variations of $\rho(\mathbf{r})$ which leave the total number of electrons unchanged, and the Euler-lagrange equation for this purpose is

$$\delta E_v[\rho(\mathbf{r})] \equiv \int \delta\rho(\mathbf{r}) \left\{ v(\mathbf{r}) + \frac{\delta T[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} \Big|_{\rho=\rho_{GS}} - \epsilon \right\} d\mathbf{r} = 0, \quad (25)$$

where ρ_{GS} is the exact ground state density for $v(\mathbf{r})$ and ϵ is a Lagrange multiplier to assure particle conservation. In this case the ground state energy and density can be obtained by solving the single particle equations

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) - E_j \right) \phi_j(\mathbf{r}) = 0 \quad (26)$$

$$\rho_{GS}(\mathbf{r}) = \sum_{j=1}^N |\phi_j(\mathbf{r})|^2 \quad (27)$$

$$E_{GS} = \sum_j E_j. \quad (28)$$

To match this description with the case of interacting electrons Kohn-Sham write the functional $F[\rho(\mathbf{r})]$ in the following form

$$F[\rho(\mathbf{r})] \equiv T[\rho(\mathbf{r})] + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho(\mathbf{r})], \quad (29)$$

where $E_{xc}[\rho(\mathbf{r})]$ is the so called exchange-correlation energy functional defined by eq.(29). The HK variational principle for interacting electrons is therefore

$$E_{v(\mathbf{r})}[\rho] \equiv \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) + T[\rho(\mathbf{r})] + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho(\mathbf{r})] \geq E_{GS}, \quad (30)$$

The corresponding Euler-lagrange equation is therefore

$$\delta E_v[\rho(\mathbf{r})] \equiv \int \delta\rho(\mathbf{r}) \left\{ v(\mathbf{r}) + \frac{\delta T[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} \Big|_{\rho=\rho_{GS}} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} \Big|_{\rho=\rho_{GS}} - \epsilon \right\} d\mathbf{r} = 0, \quad (31)$$

Now let us write

$$v_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} \Big|_{\rho=\rho_{GS}} \quad (32)$$

and

$$v_{eff}(\mathbf{r}) \equiv v(\mathbf{r}) + \int d\mathbf{r}' \frac{\rho_{GS}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r}). \quad (33)$$

Substituting these expressions in eq.(31) we find that has the same form as eq.(25) for non-interacting particles moving in an effective external potential $v_{eff}(\mathbf{r})$. Therefore we conclude that the minimizing density $\rho_{GS}(\mathbf{r})$ can be found by solving the single particle equation

$$\left(-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r}) - E_j \right) \phi_j(\mathbf{r}) = 0 \quad (34)$$

with

$$\rho_{GS}(\mathbf{r}) = \sum_{j=1}^N |\phi_j(\mathbf{r})|^2 \quad (35)$$

$$E_{GS} = \sum_j E_j + E_{xc}[\rho_{GS}(\mathbf{r})] - \int d\mathbf{r} v_{xc}(\mathbf{r})\rho_{GS}(\mathbf{r}) - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho_{GS}(\mathbf{r})\rho_{GS}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (36)$$

These are the so called Kohn-Sham self consistent equations. We see that if we neglect E_{xc} and v_{xc} altogether, the KS equations (34)-(36) reduces to the self consistent Hartree equations.

Again to solve these KS equations self consistently we start with a guess of the charge density ρ_{GS} . By using some approximate form for the functional dependence of E_{xc} on density, we must compute V_{xc} as a function of \mathbf{r} . The set of KS equations are then solved to obtain an initial set of KS orbital. This set of orbital is then used to compute an improved density from Eq.(35) and the process is repeated until the density and exchange correlation energy converge to within some tolerance. The electronic energy is then computed from Eq.(36).

The exact effective single particle potential $v_{eff}(\mathbf{r})$ of KS theory can be regarded as the unique, fictitious external potential which leads to the same physical density $\rho_{GS}(\mathbf{r})$ for non-interacting particle as that of the interacting electrons in the physical external potential. Also neither the exact KS orbital ϕ_j , nor energies ϵ_j have any known physical meaning except for the connection between ϕ_j and true physical density $\rho_{GS}(\mathbf{r})$ (Eq.(35)) and the fact that the magnitude of the highest occupied ϵ_j relative to the vacuum is equal to the ionization energy (9).

The KS orbital on each iteration can be computed numerically or they can be expressed in terms of a set of basis functions. Therefore by solving the KS equation we will find the coefficients in the basis set expansion. The choice of these basis sets comes with experience.

VI. LOCAL DENSITY APPROXIMATION

Several different schemes have been developed for obtaining approximate forms for the functional for the exchange correlation energy. The main source of error in DFT usually arises from the approximate nature of E_{xc} . The most widely used and most simple approximation for E_{xc} is the local density approximation (LDA) in which

$$E_{xc}^{LD} = \int \rho_{GS}(\mathbf{r}) \epsilon_{xc}[\rho_{GS}(\mathbf{r})] d\mathbf{r} \quad (37)$$

where $\epsilon_{xc}[\rho_{GS}(\mathbf{r})]$ is the exchange-correlation energy per electron in a homogeneous electron gas of constant density. In a hypothetical homogeneous electron gas, an infinite number of electrons travel throughout a space of infinite volume in which there is a uniform and continuous distribution of positive charge to retain electroneutrality (10).

Also for spin polarized systems local spin density approximation gives more satisfactory result for DFT calculation. In such a case E_{xc} is given by

$$E_{xc}^{LSD} = \int \rho_{GS}(\mathbf{r}) \epsilon_{xc}[\rho_{GS,\uparrow}(\mathbf{r}), \rho_{GS,\downarrow}(\mathbf{r})] d\mathbf{r} \quad (38)$$

where $\epsilon_{xc}[\rho_{GS,\uparrow}(\mathbf{r}), \rho_{GS,\downarrow}(\mathbf{r})]$ is the exchange-correlation energy per particle in a homogeneous, spin -polarized electron gas with spin-up and spin-down densities $\rho_{GS,\uparrow}(\mathbf{r})$ and $\rho_{GS,\downarrow}(\mathbf{r})$, respectively.

These expression for exchange-correlation energies are clearly approximations because neither positive charge nor electronic charge are uniformly distributed in actual molecules. To account for the inhomogeneity of the electron density a nonlocal correlation involving the gradient of $\rho_{GS}(\mathbf{r})$ is often added to the exchange energy (this is the so called generalized gradient approximation(GGA)). There are many other amendments to E_{xc} relative to the system that we want to solve in practice.

VII. APPLICATION

Now we see an application of DFT in calculating the energy spectrum of a Cu slab. We see that DFT gives satisfactory result of the electronic structure of the solid.

In calculating the energy spectrum we have used a program named TB-LMTO-ASA (tight binding-linear muffin tin orbital-atomic sphere approximation) program written by

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The tight binding linear muffin-tin orbital (TB-LMTO) method is a specific implementation of density functional theory within the local density approximation (LDA). In this method there is no shape approximation to the crystal potential, unlike methods based on the atomic-spheres approximation (ASA) where the potential is assumed to be spherically symmetric around each atom. For mathematical convenience the crystal is divided up into regions inside muffin-tin spheres, where *Schrödinger* equation is solved numerically, and an interstitial region. In all LMTO methods the wavefunctions in the interstitial region are Hankel functions. Each basis function consists of a numerical solution inside a muffin-tin sphere matched with value and slope to a Hankel function tail at the sphere boundary. The so-called multiple-kappa basis is composed of two or three sets of s, p, d, etc. LMTOs per atom. The extra variational degrees of freedom provided by this larger basis allow for an accurate treatment of the potential in the interstitial region.

Here I am showing the energy spectrum of Cu(111) using DFT , fig. VII.

VIII. CONCLUSION

In our discussion we saw that the electronic density is a basic variable in the calculation of electronic properties of matter. LDA and its spin analog LSDA has been remarkably successful in describing the ground state properties of a great range of physical systems. However LDA and LSDA can fail in systems, e.g., heavy fermion systems. In such systems electron-electron interaction is not negligible therefore DFT also fails cause they lack any resemblance to non-interacting electron gases.

References

- [1] L.H. Thomas, Proc. Camb. Phil. Soc. **23**, 542(1927).
- [2] E. Fermi, Atti. Accad. Nazl. Lincei, **6**, 602(1927).
- [3] P. Hohenberg et. al., Phys. Rev. **136**, B864 (1964).
- [4] W. Kohn, Nobel Lecture, Rev. Mod. Phys. **71**, 1253(1998).
- [5] W. Kohn, Proc. Int'l Scoool of Physics, Enrico Fermi, Course LXXXIX, p.4(1985).
- [6] M. Levy, Phys. Rev. A, **26**, 1200(1982).
- [7] E. Lieb, Int. J. Quant. Chem., **24**, 243(1983).

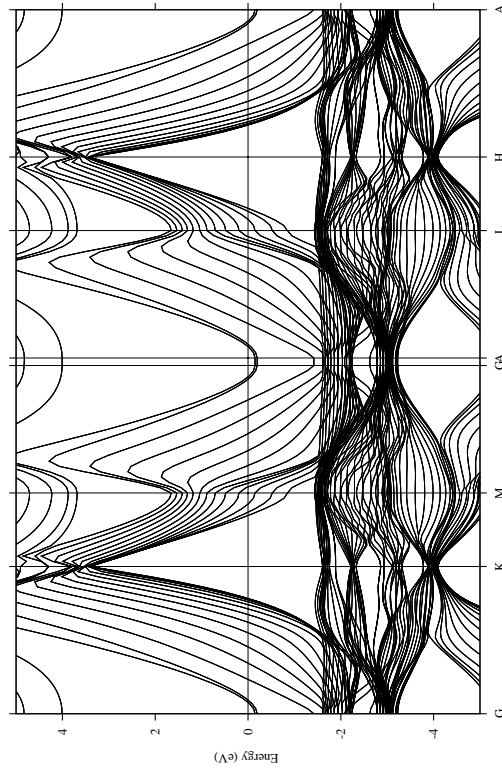


FIG. 1 Kohn-Sham energy band spectrum of a 13 layer Cu(111) slab. The Schokley surface state and the sp-band edges are indicated in the figure.

- [8] R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689(1989).
- [9] C. O. Almbladh et. al., Phys. Rev. B, **31**, 3231(1985).
- [10] An accurate expression for ϵ_{xc} is given in R.G. Parr and W. Yang, *Density functional theory of atoms and molecules*, Oxford university Press, Oxford(1989).