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SECOND EUROPEAN SUMMER SCHOOL on MICROSCOPIC QUANTUM MANY-BODY THEORIES and their APPLICATIONS

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MANY-BODY THEORY ASPECTS OF DENSITY FUNCTIONAL THEORY

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Density functional theory

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Abstract

Density functional theory is a remarkably successful theory of ordinary matter, despite its *ad hoc* origins. In these lectures I introduce the theory starting from an elementary level. The practical theory uses the Kohn-Sham equations, well-chosen energy functionals, and efficient numerical methods for solving the Schroedinger equation. The time-dependent version of the theory is also useful for describing excitations. Besides describing the methods in these lectures, I will also survey some of the many applications.

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I. INTRODUCTION

The density functional theory is now widely applied in all areas of physics and chemistry, whereever properties of systems of electrons need to be calculated. The theory is very successful in calculating certain properties–hence its popularity. This is reason enough for a student of theory to learn what it is all about. However, it is quite different in philosophy to other many-body approaches that you will hear about. The tried-and-true path in theoretical physics is to look for systematic expansions for calculating the properties of interest, finding controlled approximations that be refined to achieve greater accuracy. The density functional theory is not at all systematic, and in the end its justification is only the quality of its predictions. However, it is rightly described as an *ab initio* framework, giving theories whose parameters are determined *a priori* by general considerations. These lectures will present the theory and its applications at a pace that I hope is understandable with a minimum of prior formal training in advanced quantum mechanics. In the first lecture today, I will set the stage by deriving Hartree-Fock theory, presenting some results on the homogeneous electron gas, and finally presenting the Hohenberg-Kohn theorem, which has motivated the density functional approach.

I will begin the next lecture with a simple example of a density functional theory which can be worked out, ending up with the Thomas-Fermi theory of many-electron systems. Unfortunately, the Thomas-Fermi theory has very limited validity, and it has not been possible to make useful improvements despite many attempts. The DFT became useful only after Kohn and Sham introduced electron orbitals into the functional. In their theory the variables are the single-particle wave functions of electrons in occupied orbitals as well as the electron density. The theory then has a structure very close to mean-field theories such as the Hartree theory. The emphasis on using the density variable whereever possible leads directly to a version of the theory called the Local Density Approximation (LDA). The LDA is a significant improvement over Hartree-Fock (in ways we shall discuss), but at the same time one can see deficiencies inherent in that scheme. A more complicated implementation of the theory, called the Generalized Gradient Approximation, make it surprising accurate for calculating structures and binding energies, and in this form the theory is widely applied.

The Kohn-Sham theory requires solving the 3-dimensional Schroedinger equation many times, and questions of algorithms and numerical methods are important in making applications of the theory. There are several well-developed methods to solve the equations, and each has its advocates. In my third lecture I will discuss some of these numerical aspects. I will also survey some of the applications, noting where the DFT is reliable and where its accuracy is problematic. I will also mention some directions that have been taken to make more accurate theories, going beyond the DFT.

All of this so far is a theory of matter in its ground state. We are of course also very interested in the excitations of many-body systems, and the DFT can also be applied to dynamics, where it is called time-dependent density functional theory (TDDFT). In my fourth lecture I will derive the equations to be solved and the algorithms used to solve the equations. The time-dependent theory is quite computationally intensive, and much progress can be made by finding more efficient numerical techniques. Finally, in the last lecture, I will show you some state-of-the-art applications of the TDDFT.

Although it is not really necessary for my lectures, I will use a second-quantized field operator notation because it is the most efficient way to write down expectation values in many-particle spaces. Let us start with the basic Hamiltonian, which can be taken as the sum of three terms,

$$H = \int d^3r \frac{\hbar^2}{2m} \nabla\psi^\dagger(\mathbf{r}) \cdot \nabla\psi(\mathbf{r}) + \frac{1}{2}\int d^3r \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r}) \tag{1}$$

$$+ \int d^3r V_{ext}(\mathbf{r})\psi^\dagger(\mathbf{r})\psi(\mathbf{r}').$$

The terms represent the electron kinetic energy, the electron-electron interaction, and the interaction of the electrons with an external field, respectively. The $\psi^\dagger$ and ψ are field operators with the Fermion anticommutation relations, $\{\psi^\dagger(\mathbf{r}), \psi(\mathbf{r}')\} = \delta(\mathbf{r}-\mathbf{r}')$. I will explain what one needs to know about these as we go along. As a warm-up to the theory, I will derive the Hartree-Fock theory. But before that, some issues of notation and units should be clarified.

A. Units and notation

In eq. 1 we used units in which e^2 has dimensions of energy-length. If you are used to the MKS system, you can convert formulas by the substitution $e^2 \rightarrow e^2_{MKS}/4\pi\epsilon_0$. One often sees formulas quoted in atomic units, with no explicit dimensional quantities. In atomic units, lengths are expressed in units of the Bohr, $a_0 = \hbar^2/me^2 = 0.529..$ Å and energies in units of the Hartree, $e^2/a_0 = 27.2.$ eV. Confusingly, one also sees energies quoted in Rydbergs, $e^2/2a_0 = 13.6..$ eV. Personally, I do not care for implicit atomic units because they hide the functional dependence on mass and charge. It is also common to expressed densities in terms of the parameter r_s, defined as the radius in atomic units of a sphere whose volume is the reciprocal density. Thus $r_s = (3n/4\pi)(1/3)\hbar^2/me^2$, where n is the density of electrons. In presenting numerical results, I will often use "practical atomic units", taking eV for energy and Å (0.1 nm) for length.

B. Hartree-Fock theory

Hartree-Fock theory is very simple to describe: it is the variational theory obtained by the expectation value of the Hamiltonian, allowing all wave functions that can be represented as Slater determinants. Let's see how this comes about. Using second-quantized notation, the Slater determinants constructed from a set of orthonormal single-particle wave functions a are represented by a product of creation operators $c\dagger$ acting on the vacuum. An N-particle state is thus

$$|N\rangle = \sum_a^N c_a^\dagger|\rangle.$$

The operators $c\dagger$ and c satisfy the anticommutation relation $c_a^\dagger, c_{a'} = \delta_{a,a'}$. To to get back the orbital wave function in position space, i.e. to reveal the spatial wave function $\phi_a(r)$, we apply the field operator $\psi(\mathbf{r})$ to the state a. The anticommutator gives the sought amplitude,

$$\{\psi(\mathbf{r}), c_a^\dagger\} = \phi_a(\mathbf{r}).$$

We now take the expectation value of H in the state $|N\rangle$ and reduce the operator expection values by moving annihilation operators to the right and creation operators to the left with the help of the above anticommutators. The result at the end is

$$\langle N|H|N\rangle = \sum_a^N \frac{\hbar^2}{2m}\int d^3r\nabla\phi_a^*\cdot\nabla\phi_a + \sum_{a<b}\int d^3r\int d^3r'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}|\phi_a|^2|\phi_b|^2 \qquad (2)$$

$$-\sum_{a<b}\int d^3r\int d^3r'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_a^*(\mathbf{r})\phi_a(\mathbf{r}')\phi_b^*(\mathbf{r}')\phi_b(\mathbf{r}) + \sum_a\int d^3rV_{ext}(\mathbf{r})|\phi_a|^2.$$

The result looks very similar to eq. (1) with respect to the kinetic energy and the external potential energy terms. But the electron-electron interaction has given rise to two terms, the direct (or Hartree) energy, and the exchange (or Fock) energy. Notice also that the factor of 1/2 in eq. (1) has disappeared; instead one has a double sum over the $N(N-1)/2$ orbital pairs (a,b). It is often convenient to rewrite eq. (2) rearranging the sums slightly. Let us add terms with $a=b$ to the direct and exchange sums. This won't affect the result, because the direct and exchange cancel if the two orbitals are the same. The direct term can then be written as an independent sum over the a and b orbitals. Defining the single particle density $n(\mathbf{r}) = \langle N|\psi^\dagger(\mathbf{r})\psi(\mathbf{r})|N\rangle = \sum_a^N|\phi_a(r)|^2$, the direct and external field terms are seen to depend directly on $n(r)$. The full expectation value becomes

$$\langle N|H|N\rangle = \sum_a^N \frac{\hbar^2}{2m}\int d^3r\nabla\phi_a^*\cdot\nabla\phi_a + \frac{1}{2}\int d^3r\int d^3r'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}n(\mathbf{r})n(\mathbf{r}') \qquad (3)$$

$$-\sum_{a<b}\int d^3r\int d^3r'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_a^*(\mathbf{r})\phi_a(\mathbf{r}')\phi_b^*(\mathbf{r}')\phi_b(\mathbf{r})$$
$$+\int d^3rV_{ext}(\mathbf{r})n(\mathbf{r}).$$

Now that we have the Hartree-Fock energy function, the next task is to find the minimum within the allowed variational space. First let us recall quickly how variational principles work. If we have a integral expression $\int F(\phi)dx$ that depends on a function $\phi(x)$, the conditional that the value is stationary with respect to variations in ϕ is

$$\frac{dF}{d\phi}=0.$$

This must be satisfied for all values of x. If there is a constraint that some other integral $\int G(\phi)dx$ has a fixed value, the stationary condition contains the constraint as a Lagrange multiplier,

$$\frac{dF}{d\phi}+\mu\frac{dG}{d\phi}=0.$$

We now apply this to the Hartree-Fock energy, eq. (2), varying with respect to a wave function amplitude ϕ_a^*. Remembering that the wave functions were assumed to be normalized, we impose the constraint $\int\phi_a^*\phi_a d^3r=1$ with a Lagrange multiplier. The multiplier will be denoted ϵ_a; it looks exactly like the energy in the Schrödinger equation. The wave functions also have to be orthogonal as well, but it turns out that it is not necessary to put in Lagrange multipliers to satisfy that condition. There is one more technical point in carrying out the variation. When the gradient of a function is varied, one first integrates by parts to move the gradient elsewhere in the expression. One must impose suitable boundary conditions on the function to carry out the integration by parts, and that must be remembered in solving the differential equations that result from the variation.

Without go through the steps I will just quote the result here. One obtains N equations for the amplitudes ϕ_a,

$$-\frac{\hbar^2}{2m}\nabla^2\phi_a(\mathbf{r})+\int\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}n(\mathbf{r}')d^3r'\phi_a(\mathbf{r})-\sum_b\int d^3r'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_a(\mathbf{r}')\phi_b^*(\mathbf{r}')\phi_b(\mathbf{r}) \qquad (4)$$
$$+V_{ext}(\mathbf{r})\phi_a(\mathbf{r})=\epsilon_a\phi_a(\mathbf{r}).$$

These are the Hartree-Fock equations. It is interesting to see how well they do in making a theory of matter. In Table I is shown some energies calculated with eq. (4), taken from refs. [26, 27]. The entries in the table are atomization energies, which is the energy require

TABLE I: Atomization energies of selected molecules

	Li_2	C_2H_2	20 simple molecules (mean absolute error)
Experimental	1.04 eV	17.6 eV	-
Theoretical errors:			
Hartree-Fock	-0.94	-4.9	3.1
LDA	-0.05	2.4	1.4
GGA	-0.2	0.4	0.35
τ	-0.05	-0.2	0.13

to pull the cluster or molecule apart into individual atoms. Results are given for a simple atomic cluster, a simple molecule, and a set of molecules that are used as a testing ground for better theories. The mean absolute error in the atomization energies (energy difference between the molecule and the individual atoms in isolation) is 3 eV in the Hartree-Fock theory. The predicted binding of the Li_2 clusters is a factor ten too low, and another alkali metal cluster not in the table, Na_2, is incorrectly predicted to be unbound. We conclude that on a practical level Hartree-Fock is not accurate enough to be useful for chemistry or for computing cluster structures.

C. Homegeneous electron gas

We will see next time that the density functional theory makes use of the properties of the homogeneous interacting electron gas, and it will be useful to have on hand some analytic results. There is a systematic expansion of the energy of an electron gas accurate at high density. The first two terms are contained in the Hartree-Fock theory. They are the the kinetic energy of a free Fermi gas, and its exchange energy. As part of the warmup, I will now derive them.

1. *Free electrons*

For the free electron gas eq.(4) is solved without the potential energy, and in a box (a cube of side L) with periodic boundary conditions. Since the Hamiltonian contains only the one-particle kinetic energy operator, the equation is separable into N one-particle problems. The solution are plane waves with discrete wave vectors $\mathbf{k}$ chosen to fullfill the boundary conditions $\phi(x+L,y,z)=\phi(x,y,z)$, etc.,

$$\phi_{\mathbf{k}}(\mathbf{r}) = L^{-3/2}e^{i\mathbf{kr}} \qquad \text{where} \qquad \mathbf{k} = \left(\frac{2\pi}{L}\right)\begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} \qquad n_i = 0, \pm1, \pm2, ... \tag{5}$$

According to the Pauli Principle each $\mathbf{k}$-vector can be occupied by two electrons. Thus the volume in k-space required for one electron is

$$V_k^0 = \frac{1}{2}\left(\frac{2\pi}{L}\right)^3 \tag{6}$$

and a sum over states can be replaced by an integral over $\mathbf{k}$ according to

$$\sum_{\mathbf{k}} \to 2L^3 \int \frac{d^3k}{(2\pi)^3}.$$

The kinetic energy of a particle of wave vector $\mathbf{k}$ is given by $\epsilon_{\mathbf{k}} = \hbar^2k^2/2m$. Clearly the lowest energy state for a given number of electrons requires that the states are filled within a sphere in k-space, the Fermi sphere. Calling the radius of the sphere the Fermi wave number k_F, the number of particles can be expressed

$$N = 2L^3 \int_{k<k_F} \frac{d^3k}{(2\pi)^3} = L^3\frac{k_F^3}{3\pi^2}$$

and the corresponding density n is given by

$$n = N/L^3 = k_F^3/3\pi^2.$$

The total kinetic energy of the electron gas is found by integrating the single-electron kinetic energy over the Fermi sphere,

$$T = 2L^3 \int_{k<k_F} \frac{(\hbar k)^2}{2m}\frac{d^3k}{(2\pi)^3} = \frac{L^3\hbar^2k_F^5}{10m\pi^2}$$

We shall later need the kinetic energy density as a function of particle density. Combining the last two equations one finds

$$t = \frac{T}{L^3} = \frac{3}{10}\frac{\hbar^2(3\pi^2)^{2/3}}{m}n^{5/3} \tag{7}$$

2. Exchange energy

We evaluate the interaction in the Hartree-Fock approximation to find the next term in the energy of the electron gas. I will assume that the system remains uniform in the presence of the interaction. In general this should not be taken for granted; just because the Hamiltonian has some symmetry does not imply that the solutions do also. For the uniform solution, the wave functions remain plane waves. The next problem is that the Hartree term diverges because of the long range of the Coulomb interaction. The remedy is to include an external field to compensate, adding a positive background charge density equal in magnitude to the electron charge density. This is called the *jellium model*; in it the Hartree term is cancelled exactly. That leaves the exchange energy given by

$$E_x = -\frac{1}{2} 2L^6 \int_{k_F} \frac{d^3k}{(2\pi)^3}\frac{d^3k'}{(2\pi)^3} \int_L d^3r \int_L d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \phi^*_{\mathbf{k}}(\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r}')\phi^*_{\mathbf{k}'}(\mathbf{r}')\phi_{\mathbf{k}'}(\mathbf{r}). \tag{8}$$

The factor of $1/2$ comes from replacing the sum over orbital pairs by an unrestricted sum over orbitals. Next to it there is a single factor of 2 for spin because the two particles exchanged have to have the same spin wave function. It is easy to see how this integral will depend on the charge and on the density without going through the details of carrying it out. First, the factors of L will cancel out when the expressions for the plane wave states are inserted. The dimensionful quantities left are the electron charge squared, e^2, and the Fermi wave number k_F. These have dimensions of energy-length and $(\text{length})^{-1}$, respectively. The only quantity that can be constructed from these with dimensions of energy density is $e^2 k_F^4$. The result of carrying out the integration must be that expression multiplied by a pure number. I won't carry out the integrals here but just give the result. The exchange energy density e_x as a function of number density is

$$e_x = \frac{E_x}{L^3} = -\frac{3}{4\pi} e^2 (3\pi^2)^{1/3} n^{4/3}. \tag{9}$$

Notice that the power of n is less than in the kinetic energy term. This suggests that the expansion one is making for the energy in terms of the density is a high-density expansion. Indeed, when one evaluates the third term in the systematic many-body theory, one finds it to be small compared to the previous terms in the high density limit. But there is a surprise at that order: the expansion is not a simple Taylor series in $1/n^{1/3}$, but is nonanalytic[1]. For

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[1] This was derived by Gell-Mann and Brueckner in 1957 [47].

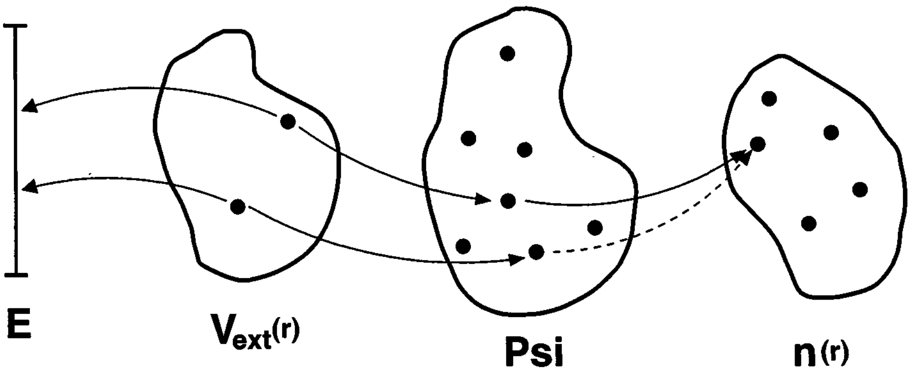

FIG. 1: Logic of the Hohenberg-Kohn theorem. The dashed mapping from a many-body wave function Ψ to a density $n(r)$ is not possible, given that another mapping exists.

future reference, I will quote the full expansion up to that order:

$$e = 2.87\frac{\hbar^2}{m}n^{5/3} - 0.74e^2n^{4/3} + \frac{e^4m}{\hbar^2}(0.033\ln(\hbar^2n^{1/3}/me^2) - 0.064) + ... \qquad (10)$$

II. WHAT IS DENSITY FUNCTIONAL THEORY?

The Hohenberg-Kohn theorem states that a variational functional exists for the ground state energy of the many-electron problem in which the varied quantity is the electron density. In this section I will go through the proof and and then give a simple example of a candidate density functional theory.

A. Hohenberg-Kohn theorem

We first separate the many-electron Hamiltonian into a part H_0 that depends only on the electron coordinates and a part V_{ext} that contains the electrons' interaction with external charges and fields. Referring back to eq. 1, H_0 contains the first two terms and V_{ext} is the last term. It should not cause any confusion to use the symbol V_{ext} both for the operator in the many-electron space and for the ordinary function of the coordinate. Let us call the ground-state wave function for this Hamiltonian Ψ. In principle we could then find the ground state energy $E = \langle\Psi|H_0 + V_{ext}|\Psi\rangle$ and the electron density in the ground state, $n(r) = \langle\Psi|\psi^\dagger(r)\psi(r)|\Psi\rangle$. These mappings are shown as the solid arrows in Fig. 1. We now ask the question of whether another Hamiltonian, differing only by the external field, could have the same ground state density. That situation would be represented by the dashed arrow in Fig. 1. This cannot happen if the ground state is nondegenerate. The proof is carried out by *reductio ad absurdum.* Suppose that a V'_{ext} and a Ψ' exist such that $n'(r) = n(r)$, with a ground state energy $E' = \langle\Psi'|H_0 + V_{ext'}|\Psi'\rangle$. If the ground state is nondegenerate, the other state must have a higher expectation value of the primed Hamiltonian,

$$\langle\Psi|H_0 + V'_{ext}|\Psi\rangle > E'$$

By adding and subtracting the expection of V_{ext} on the left hand side, it can be rewritten to put the inequality in the form

$$E + \int n(r)(V'_{ext} - V_{ext})d^3r > E'$$

In deriving this, we also made use of the assumption that $n = n'$. The same reasoning can be carried out starting from the expectation values of the Hamiltonian $H_0 + V'_{ext}$ in both states. That gives the inequality

$$E' + \int n(r)(V'_{ext} - V_{ext})d^3r > E$$

Adding the two inequalities gives

$$E + E' < E + E'$$

which is a contradiction. Thus, either the states are degenerate or $n \neq n'$. Since the mapping of Ψ into n is one-to-one into, its image in n is invertable. Let us call the functions of the image n_v (possible densities associated with Hamiltonians of the form $H_0 + V_{ext}$), and the mapping from densities back to wave functions $\Psi[n_v]$.

We are now ready for the main theorem. The Hohenberg-Kohn theorem states that the mapping of n_v to energies E defined by

$$E = \langle\Psi[n_v]|H_0 + V_{ext}|\Psi[n_v]\rangle$$

is a variational principle whose minimum is the ground state energy. Given the mappings, the proof is trivial. The energy is variational in the full space of wave functions, and thus must also be variational in a restricted space that includes the minimum. Note that the derivation gives no clue on how to construct the functional, nor does it guarentee that it is smooth enough to apply the variational equations ?? or ??.

B. A simple example: the Thomas-Fermi theory

The simplest example of a DFT, which I will now derive, is the Thomas-Fermi model electronic systems. Looking again at the HF energy function, eq. (3), we see that two of the four terms are already in the desired form, i.e. depending only on the density $n(\mathbf{r})$. These are the direct electron-electron interaction and the interaction with the external potential. That leaves the kinetic energy and the exchange energy to be approximated by a function or functional of density. The Thomas-Fermi theory emerges when we ignore the exchange energy and make the simplest possible approximation for the kinetic energy. For a slowly varying density function the kinetic energy density will only depend on the number density at the same position, Taking the specific function from the Fermi gas, eq.(7), we arrive at the kinetic energy functional

$$T[n(\mathbf{r})] = \int \epsilon(n(\mathbf{r}))n(\mathbf{r})d^3\mathbf{r} = \int \frac{3}{10}\frac{\hbar^2(3\pi^2)^{2/3}}{m}n^{5/3}(\mathbf{r})d^3\mathbf{r} \tag{11}$$

The sum of the kinetic and the potential energy terms will give us the the total energy within the Thomas-Fermi approximation,

$$E[n(\mathbf{r})] = \int \left[\frac{3}{10}\frac{\hbar^2(3\pi^2)^{2/3}}{m}n^{5/3}(\mathbf{r}) + \frac{e^2}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}' + V_{ext}n(\mathbf{r})\right] d^3\mathbf{r} \tag{12}$$

Note that the expression only depends on $n(r)$. In the next section we will apply the variational principle to find the Thomas-Fermi equation.

1. *Variational equation of Thomas-Fermi theory*

To find the ground state density function, one has to minimize the total energy functional for a fixed number of particles. This constraint is included by adding a term to the functional, $\mu \int n d^3r$, with μ the Lagrange multiplier. The variational problem is then expressed

$$\delta E[n(\mathbf{r})] = \delta \int \left[\frac{3}{10}\frac{\hbar^2(3\pi^2)^{2/3}}{m}n^{5/3}(\mathbf{r}) + \frac{e^2}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}' + V_{ext}(\mathbf{r})n(\mathbf{r}) - \mu n(\mathbf{r})\right] d^3\mathbf{r} = 0 \tag{13}$$

where the variation is to be taken with respect to n($\mathbf{r}$). Eq. ?? then gives

$$\frac{\hbar^2}{2m}(3\pi^2)^{2/3}n^{2/3}(\mathbf{r}) + e^2\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}' + V_{ext}(\mathbf{r}) - \mu = 0 \tag{14}$$

This is an integral equation for $n(\mathbf{r})$, but it can be converted into a differential equation which is easier to solve. This is done by defining a potential

$$V_e(r) = +e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'.$$

and seeing that the potential will be a solution of the Poisson equation[2],

$$\nabla^2 V_e(r) = -4\pi e^2 n(\mathbf{r}). \tag{15}$$

We first use eq. (14) to express n as a function of V_e,

$$n(\mathbf{r}) = \frac{1}{3\pi^2\hbar^3} \left(2m(-V_{ext}(\mathbf{r}) - V_e(\mathbf{r}) + \mu)\right)^{3/2} \tag{16}$$

Then substitute into the right hand side of eq. (15) to obtain

$$\nabla^2 V_e(\mathbf{r}) = -\frac{4e^2}{3\pi\hbar^3} \left(2m(-V_{ext}(\mathbf{r}) - V_e(\mathbf{r}) + \mu)\right)^{3/2}. \tag{17}$$

2. Thomas-Fermi atom

Further simplification can be obtained if particular assumptions are made for the external potential V_{ext}. For a spherical external field such as that of an atom, the potential functions will only depend on the radius. The potential of the atomic nucleus, $V_{ext}(r) = -Ze^2/r$, can be included into eqns.(16,17) to yield a general formulation valid for arbitrary atomic Z. To analyze the atomic theory, it is convenient to define a dimensionless function $\phi(r)$ according to

$$\frac{Ze^2\phi(r)}{r} = \frac{Ze^2}{r} - V_e(r) + \mu. \tag{18}$$

Then the radial Laplacian operator reduces to a simple second derivative, and eq. (14) becomes

$$\phi''(r) = \frac{4e^3 Z^{1/2}}{3\pi\hbar^3} \left(2m\phi\right)^{3/2} r^{-1/2}. \tag{19}$$

The equation for the density is the same as before; in terms of the variable ϕ it is

$$n(r) = \frac{1}{3\pi^2\hbar^3} \left(\frac{2me^2 Z\phi}{r}\right)^{3/2}. \tag{20}$$

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[2] In fact, the Poisson equation would be obtained immediately if one started from an energy function that has an explicit term for the electrostatic field energy.

These equations can be found in textbooks as the general Thomas-Fermi equations for atoms. By taking into account that the electron potential must be finite at $r = 0$ one can fix one initial condition for ϕ, $\phi(0) = 1$. Since it is a second-order equation, another condition must be imposed. In practice one makes a guess at the initial slope $\phi'(0)$, integrates to large r, sees what the solution looks like. There are three cases to be considered. The first is that ϕ remains positive and finite over the whole range of r up to infinity. This is unphysical because eq. (20) would imply that the electron density was finite everywhere. The next possible is that ϕ goes through zero at some point r_0, implying (eq. (20) again) that $n(r_0) = 0$. We can assume that the density remains zero for larger radii. Let us integrate the density to get the total number of electrons N,

$$N = \int_{r_0} n(\mathbf{r}) d^3\mathbf{r}. \tag{21}$$

Then the potential outside of r_0 must be Coulombic and given by $-(Z-N)e^2/r$. Matching at r_0 gives the value of the chemical potential,

$$\mu = -\frac{(Z-N)e^2}{r_0}. \tag{22}$$

This defines the Thomas-Fermi model of an atom with N electrons and atomic number Z. The chemical potential is negative, implying that $N < Z$.

The last case in integrating the Thomas-Fermi equation is the boudary situation where the function ϕ only goes to zero asymptotically at large r. The chemical potential is zero in this case, and the integral of the electron density is equal to the nuclear charge. This defines the Thomas-Fermi theory of the neutral atom.

In all cases the Thomas-Fermi equations require a numerical solution. Not even in the neutral-atom case it can be calculated analytically. However, eq. (19) has one very nice feature for that case. Namely, there is no finite r_0 to fix the dimension of the atom, and all of the dimensional information is contained in the coeffient on the right hand side. The equation assumes the dimensionless form $\phi''(x) = \phi^{3/2}(x)$ if we make the change of variable to $r \to (3\pi/4)^{2/3}(\hbar^2/2me^2)x$. in eq.(19). Thus all neutral atoms are described by the same universal function $\phi(x)$.

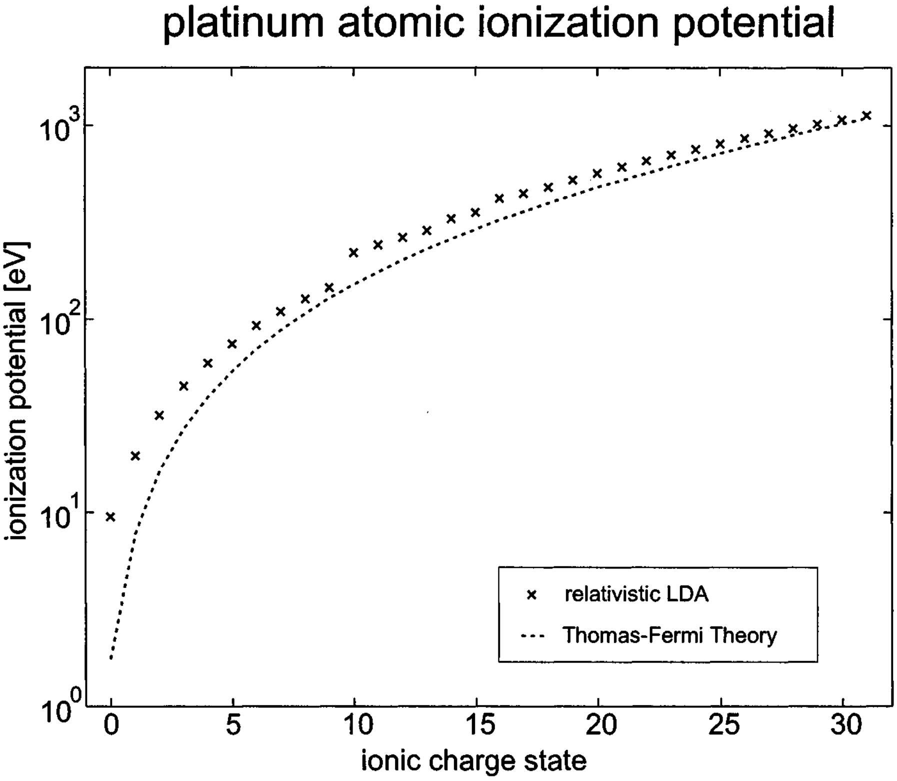

FIG. 2: Comparison of ionization potentials of platinum atoms. Dotted line is the Thomas-Fermi prediction; crosses mark the values from the Dirac-LDA theory.

3. *An example*

Let us see how well the Thomas-Fermi theory does for a heavy atom. I take as an example the Pt atom which has $Z = 78$. We will examine the ionization potentials starting from the neutral atom and going up to a charge $Q = Z - N = 30$. The Thomas-Fermi calculations are done in the way described in the previous section: one tries an initial condition, integrates, examines the charge, and from that refines the initial condition. For a give charge N the total Thomas-Fermi energy can be computed using the energy function eq. (12). The ionization potential of the ion is defined as a difference in the total energies; for charge Q $IP = E(N = Z - Q) - E(N = Z - Q - 1)$. Of course in the Thomas-Fermi theory N is a continuous parameter; we simply take the energy at the integer values. Experimentally, one only knows the ionization potentials for a few charge states. So for comparison purposes we also calculated the values using the more sophisticated Dirac-Hartree-LDA theory. The results are shown in Fig. (2). We see that the results come out quite well for high charge states, and the overall trend is reproduced. However the first ionization potential comes out poorly. Experimentally it is 9.0 eV and in the relativistic Hartree-LDA theory it is 9.5 eV, but in the Thomas-Fermi it is predicted to be only 1.8 eV.

Another failing of the Thomas-Fermi model is the complete absence of atomic shell effects. It may be see in the Figure that there is a jump in ionization potentials between charges $Q = 9$ and $Q = 10$. This is due to the depletion of the $5d$ shell and the beginning ionization of the $5p$ shell. Shell effects such as this are in fact beyond the scope of theories that ignore the the wave character of quantum mechanics. Thomas-Fermi theory fails on another fundamental property of many-electron physics, namely the existence of molecules. It can be shown (ref. [1]) that all molecules would be unstable with respect to dissociation into isolated atoms, according to the energies calculated in the Thomas-Fermi theory. Again, this points to the need for explicit wave function mechanics. From the Figure one can also see that the Thomas-Fermi systematically underpredicts the ionization potentials. This is a difficiency that can in principle be remedied by the use of a more sophisticated energy function. We shall return to this point later.

III. KOHN-SHAM THEORY

We saw in the previous section that explicit quantum mechanics is needed to make a theory that would reproduces the of the most elementary properties of matter. Kohn and Sham proposed, in essence, to put wave mechanics into the kinetic energy functional, but retain the density variable $n(\mathbf{r})$ elsewhere. Hartree-Fock theory gives us guidance on how to proceed. We take as the primary variational functions the orbitals of the Hartree or Hartree-Fock theory, and we calculate the kinetic energy accordingly. We also use these orbitals to determine the density. The interaction terms that can be expressed directly in terms of the density we keep, and we add another term, the exchange-correlation energy E_{xc} to take care of everything else. The resulting functional is

$$E_{KS}[\phi_1 ... \phi_N] = \sum_a^N \frac{\hbar^2}{2m} \int d^3r \nabla\phi_a^* \cdot \nabla\phi_a + \frac{1}{2}\int d^3r \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} n(\mathbf{r}) n(\mathbf{r}') + E_{xc}[n]$$

$$+ \sum_a \int d^3r V_{ext}(\mathbf{r}) |\phi_a|^2.$$

which is used together with the definition

$$n(\mathbf{r}) = \sum_a^N |\phi_a(\mathbf{r})|^2.$$

A. Local density approximation

Kohn and Sham proposed to treat the term E_{xc} as a simple integral over an energy density $e_{ex}(\mathbf{r})$, which in term is taken as an ordinary function of the local density, i.e. $e_{ex} = f(n(\mathbf{r}))$. This is called the local density approximation (LDA). The obvious choice for the function f is the corresponding energy density of the uniform electron gas. Since the kinetic energy is treated separately, the exchange-correlation energy is what is left over after taking away the first term in eq. (10). In fact, the idea to take the exchange energy from the electron gas was first attempted by Slater. Starting from the Fermi gas exchange energy density in eq. (9). Slater proposed to make a local density approximation by defining a two-body contact interaction that would have the same energy density. Taking an interaction of the δ-function form $V(\mathbf{r}-\mathbf{r}') = v_0\delta(\mathbf{r}-\mathbf{r}')$, the many-body interaction energy density would be $v = 1/2v_0n^2$. Comparing with the required energy density associated with the exchange, Slater added to to the Hartree Hamiltonian a two-particle contact interaction with a strength given by $v_0 = 3e^2(3/\pi)^{1/3}n^{-2/3}/2$. Then the Schrödinger equation would have an additional potential term given by

$$V_{Slater} = -\frac{3e^2}{2\pi}(3\pi^2 n_e(r))^{1/3}.$$

THIS IS WRONG. Going back to the variational principle, one sees that the one-body potential should be defined by the variation of E_{xc}, i.e.

$$V_{xc}(r) = \frac{\delta e_{xc}}{\delta n} = -\frac{e^2}{\pi}(3\pi^2 n_e(r))^{1/3}. \tag{23}$$

This is a factor 2/3 different from Slater's potential.

In practice, the LDA density functional theory takes the exchange-correlation energy from numerical calculations of the interacting electron gas. Many-body theory gives a few terms of the high-density expansion, but only numerical methods are reliable for the lower densities of interest. The classic reference is the Green's function Monte Carlo calculation of Ceperley and Alder [52], who gave a table of energies of the homogeneous electron gas. After subtracting the kinetic energy of the free Fermi gas, the function is parameterized in a way suitable for taking the derivative needed in eq. 23. Such parameterizations give the "LDA" functional of density functional theory. It gives a considerable improvement over Hartree-Fock, as may be seen by the entries in Table 1. Alkali metal clusters have reasonable binding energies, and the errors in the atomization energies decrease by a factor of two. But this is stil not accurate enough for chemical modeling.

B. Spin and the local spin density approximation

Up to now we have assumed that the electrons are all paired in the molecular orbitals: the electron density was calculated assuming two electrons occupy each spatial orbital, and the exchange-correlation energy was fit to the energy of an electron gas with equal number of up and down spin electrons. There is no reason why we can't treat up and down electrons separately, generalizing the theory to treat two (variationally) independent densities. Thus we define spin-up and spin-down densities $n_\uparrow, n_\downarrow$, and construct an exchange-correlation energy depending on both. The exchange part of the interaction is between electrons with the same spin projection, so the corresponding energy functional is a sum of two terms. Going through the same procedure we did to find the exchange interaction before, one finds the for the exchange energy density

$$e_x = -\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3} e^2 (n_\uparrow^{4/3} + n_\downarrow^{4/3}) \tag{24}$$

The correlation energy of a spin-polarized electron gas has also been calculated and fit. The parameterization of Perdew and Zunger [48] is often used; the spin-dependent correlation energy is about half the size of the spin-dependent exchange energy, for densities in the range of those occurring for conduction electrons in metals.

Eq. 24 has one feature that is obviously unphysical: it is not invariant under rotations. Suppose we have a system with the electrons polarized in the x-direction. The electron wave function then has equal amplitudes of up and down spin, and the spin-up and spin-down densities are equal. Thus the formula would treat this incorrectly as an unpolarized system. This can be easily fixed by taking as density variables the entire spin density matrix[49]. The eigenvalues of the matrix are invariant under rotations, and the energy functional depends only on the eigenvalues. I will show an application later on.

C. The generalized gradient approximation

An obvious problem of the LDA is that the single-particle potential does not have the correct asymptotic behavior. The electron potential in a neutral cluster should behave as

FIG. 3: Self-interaction.

TABLE II: Atomic properties of the Ag atom in LDA.

	IP	First excitation
Experimental	7.75	3.74
Kohn-Sham:		
eigenvalues	$\epsilon_s = 4.6$	$\Delta\epsilon = 3.9$
total energies	8.0	4.1

$-e^2/r$ for large separation of the electron from the cluster. But in the LDA the Coulomb potential is calculated with all the electrons and thus vanishes outside the cluster. This makes the LDA unreliable for calculating ionization potentials from the Kohn-Sham eigenvalues.

There is another argument why one should not trust the absolute numbers of the Kohn-Sham eigenvalues. Let us imagine starting with the full normalized wave function of a particle in its orbital, and take away probability a little bit at a time. Since quantum mechanics is a linear wave theory, the energy cost is the same to take a way a bit of the probability, independent of how much has been taken away already. But the self-interaction and exchange terms are nonlinear functions, and the energy in the Kohn-Sham theory does depend on how much probability is left[3]. This function behaves as sketched in Fig. (3). The physical energy is the difference between the values at probability $P = 0$ and $P = 1$. But the contribution to the Kohn-Sham eigenvalue is the slope at $P = 1$. It is much larger than the finite difference.

As an example of how this works out in a physical example, we calculated the ionization potential of the silver atom both ways. According to Hartree-Fock theory, the Ag atom has a single electron in an s orbital, with an unoccupied p orbital just above and a fully occupied d orbital just below. Thus the IP should correspond to the energy of the s-orbital. Table II the experimental ionization potential (IP) compared to the Kohn-Sham eigenvalue. You see that it is predicted to be more weakly bound than is the actual IP, and the error is quite

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[3] This gives rise to a real pathology of the LDA functional, that a free electron comes out to be self-bound in its exchange potential

large (40%).

What about the other method? The line labeled "total energies" was calculated as a difference between energies of the neutral atom and the singly-charged ion, i.e.

$$IP = E(\mathrm{Ag}) - E(\mathrm{Ag}^+). \tag{25}$$

The table shows that the error is only 3% when the IP is calculated this way.

Becke [30] proposed a fix to get the $-e^2/r$ asymptotic potential by adding a term to the energy functional that depends on the gradient of the density, $\nabla n_e(r)$. His proposed form works amazingly well. This is the "generalized gradient approximation", GGA. From Table 1, we see that energies can be calculated to an accuracy of tenths of an eV. Further improvements may be possible. The Kohn-Sham energy functional depends on the nonlocal quantity

$$\tau = \sum_i |\nabla\phi_i|^2$$

in the kinetic energy term. One could think of using other functional dependencies on τ; an example is given in the last line of Table 1.

The functional that is most popular in quantum chemistry is called the "B3LYP". Its popularity derives in part from the fact that it is a option in a widely distributed computer program for quantum chemistry calculations. Unfortunately, the prescription is quite *ad hoc*, taking pieces from many sources include Hartree-Fock, the local spin density approximation, and the GGA. It is not even easy to find its definition without going to the original literature for the individual terms (e.g. ref. [57]).

Later on, I will show some calculations that use the GGA prescription of van Leeuwen and Baerends [79]. They write the exchange-correlation potential as

$$v_{xc}(\mathbf{r}) = -\beta n^{1/3}(\mathbf{r})\frac{x^2(\mathbf{r})}{1 + 3\beta x(\mathbf{r})\sinh^{-1}(x(\mathbf{r}))}$$

where $x = |\nabla n|/n^{4/3}$.

IV. NUMERICAL METHODS FOR THE KOHN-SHAM EQUATION

The DFT is conceptually quite simple, but its success is in part due to the development of efficient methods to solve the Kohn-Sham equations. The algorithms may be classified by how the orbital wave function is represented. The traditional approach in quantum chemistry is to use a basis set of analytic functions centered on each atom. Gaussian basis sets are very popular because the Coulomb integrals can be evaluated exactly. Such representations have several disadvantages, however. The basis is not orthogonal, which makes it somewhat inconvenient to use. To establish convergence one has to have the flexibility to add additional functions, and this may not be easy to do, for example when one is described weakly bound electrons. The other kind of representation is to use plane waves, i.e. a mesh in momentum space, or a mesh in coordinate space. These representations suffer from the disadvantage that the granularity of the needed mesh is very different close to the nuclei than far away. It is not yet practical to deal with the full range of energy scales in the atomic problem with a uniform mesh. The way out for condensed matter theorists is to replace the nuclear potential by a much smoother pseudopotential, so that a relatively coarse grid can be used everywhere. There is much art to the construction of pseudopotentials, and I will not discuss them in detail. A popular prescription for constructing pseudopotentials was formulated in ref. [58]; a program to generate pseudopotentials this way can be download from the web site `http://bohr.inesc.pt/ jlm/pseudo.html`. Another more recent prescription together with tables of the pseudopotential parameters can be found in ref. [59].

It is very useful to understand the computation cost of of the various algorithms for solving the equations. To quantify that as much as possible, I have defined some numerical quantities in Table III. Quantities which increase with the size of the system are denoted by the symbol N with some subscript. Other quantities which may be large but are independent of the system size are denoted by the symbol M.

Part of solving the Kohn-Sham equations is to construct a potential V_e for the electron-electron interaction, given the density $n(\mathbf{r})$. This requires solving the Poisson equation, for which several methods are available. Very straightforward is to use the Fast Fourier Transform. This converts a function represented on a real space grid to the Fourier space, and it requires about

$$5N \log_e N$$

floating point operations to make the three-dimensional transform, with N the number of points in the grid. Let us call the transform $\tilde{\phi}(k) = F(\phi(r))$. Then the Poisson equation

$$\nabla^2 \phi = -4\pi n$$

TABLE III: Symbol definitions for quantities pertaining to the computational effort required by the various algorithms discussed in the main text, and their values.

Symbol	Meaning	NP method	CMP method
M_T	time steps	10^4	-
M_ω	number of frequencies	-	10
M_H	nonzero elements in H matrix row	100	-
M_{it}	iterations in conjugate gradient method	-	-
N_ϕ	dimension of vector representating ϕ		
$N_{\mathbf{r}}$	real-space points	$17,000$	-
$N_{\mathbf{k}}$	reciprocal-space points	-	9,771
N_e	number of electron orbitals (occupied states)	4	4
N_c	unoccupied states	-	320

is solved by the formula

$$\phi = F^{-1}\left(4\pi\frac{F(n)}{k^2}\right),$$

requiring 2 FFT's per cycle. As its name implies, the FFT is fast. But it also has some disadvantages. The full efficiency is available only for particular meshes; the largest routinely in use is $(128)^3 \approx 2 \times 10^6$ points. Also, the finite Fourier transform requires the system to be periodic. This is no problem for the condensed matter theorists calculating properties of crystals, but for finite systems the spurious "superlattice" sometimes requires one to use large boxes that would be the case for a finite system. For ways to cope with this problem, see ref. [80].

There is another method that is well suited to finite systems, and is also very fast. That is the *multigrid method*, which you can find described in textbooks [62] or in a review article on numerical methods for density functional theory [63]. In practice, it is found to have about the same speed as the FFT [63].

Given the Hartree potential, the next task is to solve the three-dimensional Schrödinger equation. With the large dimensions of the spaces required to represent the wave functions, only iterative methods are practical. These operate by refining the wave function. At the heart of any method is the operation of applying the Hamiltonian operator to a wave function. As a matrix multiplication, the operation requires of order N_ϕ^2 floating point operations per wave function. Taking into account that the number of electrons grows with the size of the system, the operation scales with system size as $N_e N_\phi^3$. This would be very slow in practice. There are several algorithms that only require of the order of N operations per electron.

The one used by Chelikowsky et al. [?] and by Yabana and Bertsch [9] takes advantage of the coordinate space representation. The potential is local or nearly local, so it only takes $N_\mathbf{r}$ operations to construct the vector $V\phi$ starting from V and ϕ as separate $N_\mathbf{r}$-dimensional arrays. The kinetic energy is represented as a difference operator, which is a sparse matrix in the $\mathbf{r}$-representation. The operational count is thus $N_\mathbf{r} M_H$ where M_H is the number of nonzero rows in the Hamiltonian.

The FFT is also used in many programs. In what is called the split operator technique, the potential energy is evaluated in coordinate space and the kinetic energy in Fourier space.

One also has a choice of methods for the iterative refinement of the wave function. The two main methods are the imaginary time propagation and the conjugate gradient method. The imaginary time propagation simulates the operator $\exp(-\tau H)$, which, when applied to a state will damping the higher energy components and enhance the lower energy components.

It is helpful to precondition the new vectors. This is most easily done in wave vector space, but it has been applied also in real space using multigrid method (see ref. [60]

The conjugate gradient method is a workhorse for any kind of problem with many variables and equations to be satisfied simultaneously.

Besides the iteration to get the wave function, there is an iteration on the potential.

I give as an example the calculation of the ground state of a ring of 20 carbon atoms using the Yabana-Bertsch code. The numerical parameters for the calculation are very simple: the mesh spacing, which is 0.3 Å, and the total number of mesh points, which was ??. The number of electron orbitals in this case is 40, each doubly occupied to make 4 electrons per carbon atoms. These are the valence electrons; the 2 $1s$ electrons are only including implicitly in the definition of the pseudopotential.

V. APPLICATIONS

A. Silicon and Iron

B. Vibrations

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VI. CAN WE REALLY IGNORE CORRELATIONS?

A. Van der Waals interaction

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VII. TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

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B. Numerical aspects

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3. Real time method

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A. Optical properties

1. Alkali metal clusters

2. Silver clusters

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