Chapter 8 Theoretical Model of Dense Plasmas



Abstract In the dawn of quantum mechanics, scientists had challenged to formulate the equation of many-electron system, such as atom and solid matter, just after the success of Schrodinger equation to explain a hydrogen atom. It is found, however, that a system of multi-electron requires the self-consistent treatment of exchange interaction stemming from Pauli exclusive principle.

In 1930s, Hartree and Fock has derived the equation with use of Slater determinant. It is called Hartree-Fock (HF) equation. This is the equation for many-electron system and if we can solve it, almost exact solution is obtained. However, it was difficult to solve it analytically and numerically. Scientists proposed a variety of approximate theoretical models to solve such many-electron system.

Slater has proposed screened-hydrogenic model (SHM) in 1930. Thomas and Fermi have proposed a statistical model, now called Thomas-Fermi (TF) model. These two models have been widely used, modified, extended, and applied to many purposes even now. Their physical image is very simple and useful as comprehensive understanding of the physics. The examples of applications to the equation of state (EOS) for shock compression (shock Hugoniot) are explained here. Such models can be used to single atom (ion) or statistically averaged ion, so-called average ion model (AIM).

Even with the atomic data are supplied, the ionization potential depression (IPD) is essential to solve Saha equation of ionization population, especially at highdensity plasma. Thanks to a rapid progress of computer capability, even HF equation can be solved numerically in some cases. It is very hard to solve, for example, the band structure of condensed matters. Kohn-Sham proposed density-functional theory (DFT) in 1960s. DFT solves one-electron Schrodinger equation for all electrons in the self-consistent potential. It is proved that the self-consistent potential is formulated as a function of only the density profile.

8.1 Introduction

We have studied that the ablation pressure in the rage of 1–100 Mbar can be generated in solid matters, when an intense laser irradiates them. As we will see below, the solid matters are easily compressed and ionization, and the Coulomb interaction energy becomes comparable to the thermal energy of charged particles. If a matter is compressed by keeping low temperature, Fermi degeneracy of free electrons becomes dominant in its pressure. In modern physics of laser produced plasma to be generated from solids, the physics of condensed matters should be studied inter-disciplinary. How to extend the theory and computational methods in the condensed matter physics to the case with finite temperature becomes a challenging subject.

Let us briefly summarized the matter state from solid in room temperature to extremely high-density state. In laser plasmas, special wards, **warm-dense-matter** (WDM) and **high-energy-density plasma** (HEDP) are widely used to show such high-pressure matter states. It is noted that such states are also called as **non-ideal plasma**. The physics of plasma at high-density has been studied for a long time in astrophysics relating to the plasma state inside stars and interior of planets, especially giant planets such as Jupiter. Roughly speaking, it is better to relate WDM to the giant planets and HEDP to the star interior. So, this chapter is strongly related to the evolution of objects in the space and astrophysics. It is noted that HEDP has relatively long history, while WDM became popular in the last two decades.

Physical properties under high-pressure have been also studied as subject of the condensed matter physics from the beginning of quantum mechanism. Most popular topic is **insulator-metal-transition (IMT)** of hydrogen. The IMT was predicted theoretically by Wigner and Huntington in 1935 [1]. Hydrogen is the simplest atom and there have been a lot of theory and computation on IMT. Recently, thanks to the progress of high-pressure technology, it has become a hot topic to demonstrate IMT experimentally. In what follows, the readers must be careful about the definition of IMT, because the **high-pressure physics (HPP)** community tries to demonstrate IMT by keeping the temperature low as the room temperature. Using laser-driven shock waves, the pressure increase also accompanies, in general, the increase of temperature. Any matter can be conductor at high-pressure with high-temperature, because of thermal excitation to produce many free electrons, resulting high-conductivity. This is called **plasma phase transition**.

Since the quantum physics of many-body problem becomes essential to study such high-density plasmas, we need to have basic knowledge of quantum mechanics of many-electron system. In Chap. 5, single atom or ion with multi-electrons has been studied quantum mechanically. In the present chapter, not only modeling single ion but also many-ion system coupled with quantum mechanical wave functions of many electrons are required to be studied.

In Fig. 8.1, progress of supercomputer is shown. It is surprising to know that its computational speed has increased 10,000,000 times in the last 25 years. In the early time to study the many-body problem, it was hard to do it even with such supercomputer,



Fig. 8.1 Progress of supercomputer performance (Flops). The orange dots are the performance of the world-top computer the green dots are the sum of top 500 computers. Even the computer of No. 500 shows the performance of blue dots. Over the 25 years from 1995, the seven order of advancement has been achieved. The advancement of the computational speed also has changed the methods to study the plasmas. [From data in www.top500/]

while now it is already the time to challenge a big computing of many-body problems. Before such supercomputing, however, it is important to obtain the sense of physics with simpler models. In the present Chapter, mainly single ion models developed in early stage of quantum mechanics are explained. Then, it is explained how to solve "ab-initio" models of the real high-density plasma system.

8.2 Variety of Physical States of Dense Plasmas

8.2.1 Molecule and Solid

In the book by Kittel [2], the table of **bulk modulus** is given for many solid states. The bulk modulus B is the pressure defined at solid density and room temperature as

$$B = \rho \frac{\partial P}{\partial \rho} \tag{8.1}$$

The bulk modulus indicates how high pressure is necessary to compress the solid material to increase its density two times. For example, H (0.002), C (4.43), Al (0.722), Fe (1.68), and Au (1.73), where the numbers are the bulk modulus in Mbar unit.

With the bulk modulus data of the solid matters, intense laser can be used to perform experiments to study the physical properties of matters at densities higher than solids. In addition to the laser ablation pressure, such high-pressure physics has been also promoted with use of static pressure to generated in a tiny area by **diamond anvil cell (DAC)**, which is shown later in this chapter. This is complementary to the laser ablation pressure method because DAC can increase the pressure to about one Mbar keeping the temperature as low as enough to avoid temperature effect on the physical property of matter. It is noted that a single shock compression by the ablation pressure increases both of density and temperature. To study almost adiabatic compression, it is required to use a shaped pulse with continuous increase of the laser intensity as discussed in Chap. 4, which is the same technology required for the high-gain target implosion for laser implosion.

Let us consider a molecular bonding solid the simplest of which is the hydrogen solid at low temperature. A hydrogen molecule is formed by **covalent bonding** and the bonding force is due to the **exchange interaction energy** same as the parahelium electron configuration shown in Chap. 5. At room temperature, the hydrogen molecule is in gas state. The potential energy of the center of mass of two hydrogen atoms is given in Fig. 8.2 as a function of the distance of two hydrogen nuclei. In Fig. 8.2, two potential profiles are plotted for U_A with the case of two electrons with the same spins and for U_S of the case with opposite spins. U_S and U_A represent symmetric and anti-symmetric bonding, respectively. Two electron spins are the same as para-helium and ortho-helium configurations as studied in Chap. 5.

Fig. 8.2 A famous hydrogen molecule eigenenergy as the function of the molecular nuclei distance (r). Depending upon the combination of both spins, symmetric state U_s with opposite spins becomes bound state, while antisymmetric case U_A with the same spins is not bound state because of the Pauli exclusive principle



Exchange interaction is negative only for the case with the opposite spin pair, therefore, the molecule bonding is possible only for the opposite spin pair. Such covalent bonding force is strong and the dissociation energy is 4.52 eV. It suggests that high-temperature is demand to dissociate the molecule thermally.

This potential energy U(r) at T = 0 is the total energy of the hydrogen molecule, and the force F(r) to compress of the system is given as

$$F = -\frac{\partial U}{\partial r} \tag{8.2}$$

Note that the force vanishes at the equilibrium radius of the bottom of the potential as indicated at $r = r_0$ (*state* 3) in Fig. 8.2, and it is attractive for the larger distance, the states 1 and 2, and repulsive at shorter distance state 4 in Fig. 8.2. This force can be converted to the pressure for the solid with many molecules. If the average volume of one molecule is give as V, U is nothing without the internal energy of the average molecule of the thermodynamic system. By use of the relation of thermodynamics, we obtain the pressure P and the force of the molecule surface in the forms

$$dU = -PdV \implies P = \frac{\partial U}{\partial V} \implies 4\pi r^2 P = F$$
 (8.3)

This pressure is called **elastic pressure** and **cold pressure**.

The potential energy of the molecular bonding has been modeled with **Lenard-Jones potential**.

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$
(8.4)

Then, the minimum energy is $-\varepsilon$ at $r = 2^{1/6} \sigma$.

8.2.2 High-Pressure Cold Matters

Let us call the high-pressure state of condensed matter at room temperature or less as high-pressure cold condense matter or simply **high-pressure cold matter (HPCM)** in this Chapter. In Fig. 8.3, a conceptual diagram of the change of states and physical phenomena are shown. Decreasing the temperature of hydrogen gas, hydrogen liquid and solid is formed at very low temperature 14 K. The binding between the molecules is not covalent bonding, but the **dipole-diploe interaction** schematically shown in Fig. 8.4. The electron cloud in each molecule shifts so that each molecule has dipole moment of charge. This bonding is week compared to the covalent bonding. Such force is called **Van der Waals force** and it is also modeled with Lenard-Jones potential force in (8.4) with appropriate parameters ε and σ .



Fig. 8.3 Schematic diagram of temperature and density showing the phase transitions in the different regions produced by intense laser irradiation on solid materials. The ablating plasma with green color finally becomes ideal plasma expanding to the vacuum. The shock compression of solid change the state of matter to strongly coupled plasma as shown in red. In HPP, metallic hydrogen has been studied by applying high-pressure without increase of temperature. This study is shown with blue lines and the point is compression without heating



Fig. 8.4 Schematics of solid or liquid hydrogen bonding. The electron cloud in hydrogen molecule shifts from the center symmetry induces the dipole field to attract the other molecules via dipole interaction. In low temperature limit, they can stay as solid via this van der Waals force

8.2.3 Pressure Ionization

Using the DAC, the matter state changes as the light bule marks in Fig. 8.3, where the temperature is kept low enough. Initially, the solid hydrogen is insulator because all electrons are bounded in their parent molecules. In the word of the band theory of the solid-state physics, the electrons are all in the valence band and cannot move nonlocally. The insulator has a large band gap, and the Fermi energy is in the forbidden region as shown in Fig. 8.5. With increase of the density of the solid hydrogen, so-call **pressure ionization** mechanism becomes important. The pressure ionization makes the ionization potential depressed, and the matter state alters to semiconductor and conductor as schematically shown in Fig. 8.5.



Fig. 8.5 A picture showing the difference of three state of normal solid matters. In the band theory, the system has valence band and conduction band. Many materials in solid state are classified to three, metal, semiconductor, and insulator. Metal has free electrons in the conduction band. The conduction and valence bands are separated by a gup, while it is called the semiconductor if the band gap is smaller than 3.2 eV. For the case with more wide energy gap and no electrons in the conduction band, it is insulator



Fig. 8.6 If any atom is isolated and no effects by free electrons and nearby atoms, the energy levels of all bound electrons are affected only by the Coulomb forces by the nucleus and the other bound electrons. In solid materials and dense plasmas, the free electrons running in the atom shields the Coulomb field also the potential of the surrounding ions decrease the ionization potential. This is called pressure ionization and ionization potential lowering

Let us explain the mechanism of the pressure ionization for a simple case regarding one atom in high-density after the dissociation of molecular state. As shown on the left in Fig. 8.6, the isolated atom in neutral state has bound electrons in the grand state. The potential field can confine all bound electrons. However, with the increase of the density, the Coulomb field by nearby nuclei works to weaken the force by the central nucleus and the overlapping of the Coulomb field changes the free state energy lower than the isolated case. In addition, the free electron density at the atomic shells becomes high to shield the nuclear Coulomb potential.

As the result, the energy levels of the upper state electrons shift, and it also be broadened by the nearby nuclei and free electron fields. Many-body problem should be solved for a system made of N nuclei with N×Z electrons. Of course, it is possible to extend **Hartree-Fock method** explained in Chap. 5.3 to many-atom system formally. However, it is almost impossible to solve such many-body problem staring from total Hamiltonian to obtain the total wave function of electrons for a given positioning of all nuclei. Some challenge for solving approximated wave functions in each five-atom system has been carried out, where so called discreate-variational X α method is used to obtain total electron wave function as shown later.

Several methods have been developed to find approximated electron quantum states. There are two broad classes of methods, wavefunction-based and density-based and each of these classes are further subdivided into different approaches. These two methods are.

- Wavefunction-based methods: An explicit form for the wavefunction is written down and observables are calculated using this wavefunction. Examples are Hartree-Fock method and para-potential method as already shown in Chap. 5. More simplified para-potential method, screened-hydrogenic model (SHM) will be explained soon below. In laser produced plasmas, SHM has been widely used to make data base of thermodynamic quantities in wide range of density and temperature by including the pressure ionization effect. This idea was initially proposed by Slater in 1930.
- 2. Density-based methods: The focus is shifted from the wavefunction to the electronic density. The wavefunction is not written explicitly. Examples are Thomas-Fermi approximation and density-functional theory (DFT). In laser produced dense plasma, computer simulation based on the density functional theory has been used by coupling with molecular dynamic simulation for ion motion. Such simulation is called *Ab initio* simulation.

The high-pressure physics experiment with use of DAC can keep the temperature low enough to study the physics of condense matter at higher density than solid. The long-standing challenge is the demonstration of metallic hydrogen experimentally. Recent apparent progress on this topic is given later. In addition, finding of superconductivity in hydrogen under extremely high pressure is also reported.

The insulator metal transition of hydrogen is also very important in planet science. It is expected that the inside of giant planets such as the Jupiter and Saturn are made of hydrogen in metallic state. Like the dynamo-effect inside our Earth, a strong magnetic field can be generated by the dynamo motion in the Jupiter. Magnetic field on the Earth stems from the convective motion of melted iron inside. Since the hydrogen metal may have higher conductivity than the melted iron, roughly speaking, stronger magnetic field may be expected for the Jupiter case. About 20 times stronger magnetic field has been observed near the surface of the Jupiter, and it is predicted with the high-conducting metal of hydrogen inside the Jupiter. So, the high-pressure physics is important to study the physics of interior of giant planets, many of which have been found as outer-solar planets recently.

8.2.4 Warm Dense Matter

In Fig. 8.7, shown is the density and temperature diagram in logarithmic scale of the regions of warm dense matters (WDM) and high energy-density plasma (HED). Note that there is no common clear definition of both states of WDM and HEDP. In addition, it is also difficult to clearly define the deference of matter and plasma. Roughly speaking, the physics of high-energy density is relatively simpler than the physics of warm dense matter, because almost no idealistic theory is applicable to describe the physical property of the warm dense matter. Since the temperature is higher in HEDP compared to the WDM, HEDP is strongly related to the physics of the evolution of stars as shown in Fig. 8.7, where the evolutional paths of the Sun and a star with 60 times solar mass are plotted. In contrast, the WDM can be said to be the physics of the evolution of planets, especially giant planets as shown in Fig. 8.7, where the giant planet such as Jupiter and brown dwarf are plotted. The central core of laser fusion implosion is located above the center of the Sun.

The physics of warm dense matter is a frontier between condensed matter and plasma physics. Here the density goes around the solid density and the temperature varies from 0.1 to 100 eV. In this regime, matter is mostly degenerate, strongly coupled, and non-ideal. WDM is an interdisciplinary research field bridging



Fig. 8.7 Density and temperature diagram in logarithmic scale of the region of HED (high-energydensity) and WDM (warm dense matter), while this zoning is very ambiguous and no clear boundary in general. Reprinted with permission from Ref. [1]. Copyright by National Academies Press



Fig. 8.8 Any materials in the state of insulator at cold temperature can show the property of conductor by the increase of the high-energy tail of Fermi distribution of electrons. Such change to metal from insulator by heating is called plasma phase transition

high-pressure physics community and laser-plasma community, where the former has grown from the condense matter physics historically. From the theory point of view, one must deal with *ab initio* calculations such as **quantum molecular dynamics (QMD)** which work well at low temperatures (T < 1 eV) and density functional theory for electrons.

Different from T = 0 case, the system of many particles is not in the grand state quantum mechanically. Atoms are ionized not only by the pressure ionization, but also by the thermal ionization as shown in Fig. 8.8. Free electrons are not completely degenerated and thermal excitation produces the free electrons in conduction band. In such case with thermal excitation of the system, the electron quantum system is calculated by assuming the nuclei are fixed in time. This is called the **Born-Oppenheimer approximation**. Another way of stating this approximation is that the time scale of the motion of electrons is much shorter than the nuclei and thus the response time of the electrons to any change in the positions of the nuclei is considered immediate, namely quasi-steady-state response of electrons can be assumed. The motion of all nuclei is treated as classical Coulomb interaction system given by the electron charge distribution. This simulation is QMD.

8.2.5 High-Energy Density Plasma

When matters are compressed to the direction of the red marks in Fig. 8.3, the electron degeneracy is important even if the thermal energy of electrons are a few or several times larger than the Fermi energy. The main fusion fuel of DT should be compressed under its temperature as low as possible for the high gain fusion energy production to be discussed in Vol. 3. Such partially degenerate high-density matter is

also a target of our research. More high-density characterizing the inside of compact objects in Universe, then, **strongly coupled plasma (SCP)** should be studied. In SCP, the ion-ion Coulomb charge interaction becomes important with relatively uniform electron density background.

While there is no definitive threshold of being in the high-energy density regime, perhaps a rough measure would be material at pressures of around one megabar, which is a quantity whose units are energy per unit volume ~1 Mbar (10^5 J/cm³). For example, material at a density of 0.01 g/cm³ and heated to 100 eV is at 1 Mbar. A temperature of 100 eV corresponds to about 10^7 J/g for hydrogen.

Roughly speaking, most of the theoretical models and numerical methods used for describing WDM can be extended to HEDP. It can be said that HEDP is simpler than WDM from theoretical modeling point of view. Special case of HEDP is, for example, the matter at the center of white dwarfs. Electrons are almost completely degenerate and the ions are moving like inside the sea of electrons. Such case is modeled by **one-component plasma (OCP)** and the ion-ion Coulomb correlation is studied in the uniform electron density.

8.2.6 Ion Sphere and Average Ion Models

The concept of ion sphere model has been widely used to describe the atomic state and thermo-dynamic property of the WDM and HEDP. In this model, the **ion sphere radius** R is defined by a simple relation.

$$\frac{4}{3}\pi R^3 n_i = 1 \tag{8.5}$$

Assume that this ion sphere shown in Fig. 8.9 is not a real ion, but this sphere represents the statistically averaged ion sphere. Therefore, it gives any physical properties of the statistical averaged ions. When the physical properties stemming from the statistical distribution around this averaged state, it is required to do additional study. For example, line broadening is obtained only when the statistical distribution of ion-ion distance fluctuation is given. It is noted that many physical properties such as equation of state is approximated with the ion sphere model as shown below.

Such kind of modeling is called **average-ion-model** (**AIM**) in plasma. It is also called **average-atom model** (**AAM**). The combination of AIM and SHM have been intensively used to make data base for radiation hydrodynamic codes for laser-produced plasmas. Assuming that the ion sphere is a micro-thermodynamic system of plasma, it is possible to obtain the thermodynamic property, pressure, and internal energy as functions of density and temperature.

To provide an easy image of AIM in statistical physics, it is a good example to compared to the fluid modeling of the plasma. The plasma is defined with velocity distribution function and the best way to study the physics of plasma is to start with



Vlasov equation. However, most of plasma can be described with fluid approximation. The fluid approximation is a mathematical model to reduce the freedom of statistical system. So, the reader not familiar with such atomic physics can regard that AIM is a kind of fluid model in plasma kinetic theory.

In the case of local thermodynamic equilibrium (LTE), it is possible to obtain the Helmholtz free energy F for given (V, T), where the volume V is regarded as the volume of the ion sphere defined in (8.5).

$$\varepsilon = F + TS \tag{8.6}$$

$$S = -\frac{\partial F}{\partial T} \tag{8.7}$$

$$P = -\frac{\partial F}{\partial V} \tag{8.8}$$

It is in general possible to separate F into three components,

$$F = F_c(V) + F_e(V, T) + F_i(V, T)$$
(8.9)

This free energy F should be the same as F in (8.2) at T = 0. Therefore, $F_c(V)$ is determined by the molecular bonding and Coulomb repulsion or any bonding at T = 0 as in Fig. 8.2.

Once the free electrons appear as metallic state shown in Fig. 8.5 due to the pressure ionization by compression, the free electrons contribute to the free energy to give Fermi pressure. As we discuss later, Coulomb interaction energy becomes important in some case of WDM, the Coulomb interaction energy with the nearby ions should also be included in $F_c(V)$. How to model $F_e(V, T)$ and $F_i(V, T)$ are the main subject of the equation of states in WDM as will be seen later.

Historically, the quantum state of high-density matters has been studied by two different approaches. In the band theory, appearance of forbidden zone of a free electron in solid is clear, for example, by solving one-dimensional Schrodinger equation of an electron in a periodic potential. One example of simple theory is **Kronig-Penny model**. The other approach is mostly based on the ion sphere model. As already mentioned, there are two ways to study; namely, one is electron density-based theoretical method and the other is wave-function based method. They have been developed to obtain the free energy by electrons F_c and F_e in (8.9)

In the present Chapter, Thomas-Fermi theory is explained at first as the simplest theory for the density-based method. How sophisticated theory can be commonly used to study WDM and HEDP depends on the progress of experimental facility and diagnostics as well as computer technology. Precision diagnostics and well-defined laser experiments have recently demanded so-called *ab-initio* simulation as precise as possible to solve many-body system realized in experiments. *Ab initio* calculations are computations of electronic orbitals with no other hypotheses than Coulomb interactions between all electrons and nuclei with electrons obeying Fermi statistics with the Pauli exclusion principle.

Computer simulation of **molecular dynamics** (**MD**) is used for dense plasma instead of **particle-in-cell** (**PIC**) simulation in relatively low density hightemperature plasma. MD is originally used to solve the ion dynamics with effective potential such as Lenard-Jones potential in (8.3). Most popular example is dynamic simulation of protein folding in water molecule heat bath. On the other hand, the electron distribution in condense matters has been studied with **density functional theory** (**DFT**) for given positioning of all nuclei. The rapid progress of computing shown in Fig. 8.1 has made it possible to combine MD and DFT to know time evolution of WDM, where MD is replaced with *ab-initio* QMD.

The second method, wavefunction-based model, can give us more detail information of the electron quantum state. However, as already mentioned in Chap. 5, Hartree-Fock method can be formulated, while it is almost impossible to solve it in many-body problem. Wave-function based method results, for example, the property due to the quantum shell structure of bond electrons. In Fig. 8.10, the ionization energy needed to reach charge state Z from charge state Z-1 of a copper ion is plotted, where the color-coding indicates the valence electron shell of state Z-1. K, L, M, and N shells represent the quantum sates with the principal quantum number n = 1, 2, 3, and 4, respectively. The jump of the values in Fig. 8.10 is due to the shell structure of the wave functions. The Thomas-Fermi model cannot reproduce such shell-dependent property.

In the ion-sphere model, if we can have **self-consistent spherical potential** V(r) in the ion sphere (r < R), it is easy to solve one-electron Schrödinger equation.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi_i = E_i\psi_i \tag{8.10}$$



where ψ_i and E_i are the electron wave function and eigen-energy for a quantum state "i", respectively. It is easy to solve (8.10) numerically for a given consistent potential V(r), while to find the V(r) is a tuff job. Note that V(r) should consist of

$$V(r) = V_{ie} + V_{ee} + V_{ex}$$
(8.11)

where V_{ie} is Coulomb interaction energy with nuclear charge, V_{ee} is the electronelectron Coulomb interaction energy, and V_{ex} is the exchange interaction energy. The Hartree-Fock method is solved iteratively to obtain the total wave function in Slater matrix and all interaction energies are included consistently. However, new theoretical model is required for each of three potentials in (8.11) once Schrödinger equation is reduced to one electron equation.

In the present Chapter, we look back the para-potential method to give a consistent potential screened by many electrons in an atom. Based on the fundamental property of hydrogen atom, the method to fit the binding energy of each electron in multi-electron ion-sphere is explained. This is called screened hydrogen model (SHM) and has been widely used to obtain the thermodynamic property in laser-plasma.

It is noted that AIM gives only the physical quantity averaged over many statistical configurations is obtained. However, it is shown that how we can obtain the statistical spread of each configuration, such as charge distribution and energy shift of line emission due to the difference of the number of electrons in the same shell, is obtained by use of SHM in laser plasma as to be explained.

8.2.7 Band and Band Gap

It is better to see why bands and band gaps appear in dense-matters as quantum effect. The electrons in an atom occupy atomic orbitals, each with its own individual energy level. When two or more atoms combine to form a molecule, their atomic

orbitals overlap. In Fig. 8.11, the energy states of electrons are shown as the s-state and p-state when the interatomic distance is large, that is, the atom is an isolated atom. In the case of hydrogen molecule in Fig. 8.2, it is shown that the s-state becomes to have two energy levels because of the Pauli's exclusion principle as U_S and U_A . In a molecule, Pauli's exclusion principle states that no two electrons can have the same quantum number. Therefore, when two identical atoms combine to form a diatomic molecule, each atomic orbital splits into two molecular orbitals with different energies.

This means once the overlapping of two electron wave functions takes place at a certain interatomic distance in Fig. 8.11, the separation of the energy level of the s-state appears as well as the p-state. The electrons in the previous atomic orbitals can occupy the new orbital structure without having the same energy. Similarly, when N identical atoms are assembled to form solid, such as crystal lattice, the electron orbitals overlap over many nuclei. Due to the Pauli exclusion principle, the wave functions of two electrons cannot overlap with the same quantum number, so the atomic orbitals are split into N individual orbitals, each with different energy. This is indicated on the left in Fig. 8.11, where the band in high-density with the interatomic distance "a" is made of many of different energy levels.

Because the number of atoms in a macroscopic solid is so large $(N \sim 10^{22})$, the number of orbitals is also very large, and therefore the energies are very closely spaced. The energy of the adjacent levels is on the order of 10^{-22} eV. Since the energies of adjacent levels are very close, they can be considered as a continuum, or energy band. The formation of such bands is mostly a feature of the outermost electrons (valence electrons) of the atom, which are involved in chemical bonding



Fig. 8.11 On the right, the energy level structure change by the decrease of the interatomic distance is plotted. For the case where the atomic distance is large, the atom is isolated and fine discrete energy levels are defined. As the distance decreases, the many electrons from the surrounding atoms makes different eigen energy state like the case of hydrogen molecule in Fig. 8.2. At the solid density (radius a) or higher density, the band structure is formed. Since the band structure is formed by many electrons in the dense state, there are roughly the number of eigen states by all electrons 10^{22} cm^{-3} in unit volume in solid as shown at the left

and electrical conduction. Since the inner electron orbitals do not overlap as much, their bands are very narrow.

The band gap is the energy range that remains uncovered by any of the energy bands due to their finite width. The width of a band depends on the degree of overlap of the atomic orbitals from which the band originates. The width of two adjacent bands is insufficient to cover the full energy range. For example, the bands associated with core orbitals (such as 1s electrons) are very narrow due to the small overlap of adjacent atoms. As a result, the band gap between the core bands tends to be large. In the higher bands, the bands become progressively wider at higher energies due to the overlap of relatively large orbitals, and the band gap disappears at higher energies.

8.3 Screened Hydrogen Models

The wave quantum mechanics is found to give the precise quantum state of hydrogen atom thanks to the discovery of **Schrodinger equation** in 1926. Then, many peoples tried to extend one-electron Schrodinger equation to atoms with multi-electrons, including partially ionized atoms. In 1927, the next year, Hartree introduced so-called **Hartree method** to solve N-electron wave function in an atom. In 1930, Slater and Fock independently pointed out Hartree method did not satisfy the principle of anti-symmetry of the wave function required by the Pauli exclusive principle for Fermion electrons. In 1935, Hartree reformulated the method more suitable. Now, **Hartree-Fock method** with the wave function of the determinant of Slater matrix is widely used as very precise basic equation for multi-electron system.

Even with Hartree-Fock equation proposed in 1930s, it is almost impossible to solve it analytically and very time-consuming calculation was demanded to apply even atoms with a small number of electrons. Historically, the birth and rapid progress of computational capability has been required to solve Hartree-Fock equation. Therefore, a variety of models have been proposed in the early time by neglecting some physics elements due to multi-electron effect. By focusing on the Coulomb shielding effect in the multi-electrons bounded in an atom or ion, Slater proposed a method to obtain the eigen energy of multi-electron atom. This is the basic idea of the **Screened Hydrogen Model (SHM)** described in this section. Note that this model is still used widely after the improvement of the screening constants.

The historical development of the SHM is reviewed briefly by Smithwick in [3]. Let me borrow his sentence. The SHM is an alternative and simple approach that uses the one-electron wavefunctions of the hydrogen atom for each electron of a multi-electron atom by substituting an effective nuclear charge Z_i for the value of Z. Agreement with experimental energies can be obtained by varying Z_i with screening parameters. The SHM provides a starting point for semi-empirical calculations involving complex atomic or molecular systems.

The SHM was first used in 1930 by Slater who approximated the energies of electrons in 1s and 2s/2p orbitals as $E_i = (Z_i)^2 \frac{1}{2n^2}$ in atomic units. Z_{1s} (for $n_i = 1$) equals Z – 0.30 when two 1s electrons were present and both Z_{2s} and Z_{2p} (with $n_i = 2$) equals Z – 1.70–0.35 (N_{2S} + N_{2P} – 1) when two 1s electrons were present. The Slater 1 s wave function was the same as the hydrogen 1 s wave function with Z_{1S} substituted for Z. The Slater 2s and 2p wave functions both had the same value of $Z_{2S} = Z_{2P}$ substituted for Z and the same radial part of the hydrogen-like 2p wave function but with 2s or 2p angular parts. Numerous molecular orbital calculations were based on Slater wave functions. Layzer and Kregar each calculated screening parameters and electron energies with series functions in powers of Z.

The calculation of the properties of dense plasmas at high temperatures is an important application of the SHM that involves the determination of the energies of atoms and ions across the periodic table. The Dirac equation is an alternative form of the SHM that includes relativistic corrections for each electron. A closer agreement between experimental and calculated electron energies is expected to lead to improved predictions of plasma properties.

It is in general hard to solve *ab-initio* model such as Hartree-Fock equation in high-density plasma because it is not clear how to model the pressure ionization in Hartree-Fock method. If we have appropriate radial potential V(r) for modeling the ion sphere in any density and we can obtain reasonable wave functions to calculate not only the thermodynamic functions, the free energy $F(\rho,T)$, but also oscillator strengths of line radiations etc. Then, it is convenient for installing equation of state and opacity in simulation codes. Note that equation of state can be modeled with statistically averaged atomic state, while the opacity, especially line radiation opacity, calculation needs the variance distribution from the average atom state.

Here, only the average ion model (AIM) is discussed to obtain the equation of state such as pressure and internal energy in dense plasma. They are used in modeling in hydrodynamic simulation for laser produced plasma. This AIM is a robust model to obtain the eigen energy of any ionization state of any atom, based on the quantum theory of hydrogen atom. The energy is given by taking account of the Coulomb charge screening in multi-electron bound atom or ion.

8.3.1 Screened Hydrogen Model (SHM)

By using SHM improved by More [4], the energy of an electron in an eigen state n (the principal quantum number) is given to be

$$E_n = -I_H \left(\frac{Z_n}{n}\right)^2 + E_n^0 \tag{8.12}$$

Where I_H is the Rydberg constant (13.6 eV). In (8.12), Z_n is the effective nuclear charge seen by the electron in the state n and E_n^0 is the screening effect by the

electrons outside the orbit of the electron in the state n. In (8.12), the Z_n and E_n^0 are given to be

$$Z_n = Z - \sum_{m < n} \sigma_{n,m} P_m - \frac{1}{2} \sigma_{n,n} P_n$$
(8.13)

$$E_n^0 = \frac{1}{2} \frac{e^2}{r_n} \sigma_{n,n} P_n + \sum_{m>n} \frac{e^2}{r_m} \sigma_{m,n} P_m$$
(8.14)

where σ_{nm} is the screening constants proposed by More so that the ionization potentials of a variety of atoms are well reproduced compared to those obtained by solving Hartree-Fock Slater equation [5]. In (8.13) and (8.14), Z is the ion nuclear charge and P_n (P_m) is the number of electrons in the eigen-state n (m). In (8.14), r_n (r_m) is the effective orbit radius of the electron with the quantum number n (m) and defined as

$$r_n = a_B \frac{n^2}{Z_n} \tag{8.15}$$

where a_B is the Bohr radius.

The well-known relations of the hydrogen-like ions are explicitly used to obtain the energy E_n . The relation of SHM has an advantage for the consistency condition;

$$\frac{\partial}{\partial P_n} E_{ion} = E_n \tag{8.16}$$

where E_{ion} is the total energy of the bound electrons in the ion and is defined as

$$E_{ion} = -\sum_{n} I_H \left(\frac{Z_n}{n}\right)^2 \tag{8.17}$$

Since the electron-electron interaction energy should not be doubly counted, the following relation is required in the model.

$$E_{ion} \neq \sum_{n} E_n \tag{8.18}$$

It is convenient to use another expression of E_n^0 and Z_n in (8.13) and (8.14).

$$Z_n = Z - \sum_{m \le n} \sigma_{nm}^{AM} P_m \tag{8.19}$$

$$E_n^0 = \sum_{m>n} \sigma_{nm}^{AM} P_m \tag{8.20}$$

Table 8.1 Screening constants σ_{nm}^{AM} defined in (8.21) as a table of matrix [n, m]. The number 1–10 is this table shows "n". This means the screening effect to an electron in the n-sate by the m-state electron is large for n > m, while it is relatively small for n < m as easily understood from the spread of wave functions

n= 1	2	3	4	5	6	7	8	9	10
0.3125	0.9380	0.9840	0.9954	0.9970	0.9970	0.9990	0.9990	0.9999	0.9999
0.2345	0.6038	0.9040	0.9722	0.9979	0.9880	0.9900	0.9990	0.9999	0.9999
0.1093	0.4018	0.6800	0.9155	0.9796	0.9820	0.9860	0.9900	0.9920	0.9999
0.0622	0.2430	0.5150	0.7100	0.9200	0.9600	0.9750	0.9830	0.9860	0.9900
0.0399	0.1597	0.3527	0.5888	0.7320	0.8300	0.9000	0.9500	0.9700	0.9800
0.0277	0.1098	0.2455	0.4267	0.5764	0.7248	0.8300	0.9000	0.9500	0.9700
0.0204	0.0808	0.1811	0.3184	0.4592	0.6098	0.7374	0.8300	0.9000	0.9500
0.0156	0.0624	0.1392	0.2457	0.3711	0.5062	0.6355	0.7441	0.8300	0.9000
0.0123	0.0493	0.1102	0.1948	0.2994	0.4222	0.5444	0.6558	0.7553	0.8300
0.0100	0.0400	0.0900	0.1584	0.2450	0.3492	0.4655	0.5760	0.6723	0.7612

where σ_{nm}^{AM} is the screening constant introduced in [6]. There is a simple relation with Kronecker δ .

$$\sigma_{mn}^{AM} = \sigma_{mn} \left(1 - \frac{1}{2} \delta_{mn} \right) \tag{8.21}$$

The matrix table of σ_{mn}^{AM} is given in Table 8.1 [6].

It is important to know that the above formulation to obtain the wellapproximated energy of bound electrons can be used to any given configuration with integer n. Then, we can use the SHM for **detailed configuration accounting** (**DCA**) for all possible configurations. If we can model the transition cross sections of electron collision and photon processes as described in Chap. 5, even the photoionizing non-LTE plasma atomic process can be studied reasonably by solving the rate equations of all possible detail configurations within SHM as shown, for example, in [7].

8.3.2 Average Ion of SHM

In the case of the average atom model, the above relations to SHM are extended by assuming that the number of electrons in the n-shell is not the real number but the statistically averaged non-integer number. Of course, the relation $P_n/g_n \le 1$ should be satisfied, where g_n is the number of states of the eigen state n.

Assume the **local thermodynamic equilibrium (LTE)** condition. The electrons in an averaged ion are separated to the bound electrons and free electrons. The energy distribution of the bound electrons is assumed to be governed by Fermi-Dirac distribution.

8 Theoretical Model of Dense Plasmas

$$P_n = g_n \left[1 + exp \left(\frac{E_n + \Delta U - \mu}{T_e} \right) \right]^{-1}$$
(8.22)

where μ is the chemical potential and ΔU is the energy shift due to the **continuum lowering** as schematically shown in Fig. 8.6. To derive the continuum lowering has been performed relating to the ion state inside stars in astrophysics. Recently, it has become possible to clarify the continuum lowering experimentally to verify such theories. Here, we adopt the continuum lowering expression in high-density limit of **Steward-Pyatt model** [8].

$$\Delta U_{SP} \approx \frac{3}{2} \frac{Z^* e^2}{4\pi \varepsilon_0 R_0} \tag{8.23}$$

Note that More details are given in the next section.

We also assume that the free electrons are also in LTE, therefore, the number of free electrons per an ion is given to be

$$Z^* = \frac{1}{2\pi^2 n_i} \left(\frac{2mT_e}{\hbar^2}\right)^{3/2} I_{1/2}(\mu/T_e)$$
(8.24)

$$I_{1/2}(x) = \int_0^\infty \frac{y^{1/2}}{1 + exp(x-y)} dy$$
(8.25)

The chemical potential μ is determined so that the charge neutrality condition is satisfied.

$$Z = Z^* + \sum_n P_n \tag{8.26}$$

Assuming a certain value of the maximum of n (n_{max}) and using (8.12) and (8.26), we can obtain the statistically averaged population P_n for given density and temperature.

It is not trivial to model an appropriate value of n_{max} . The maximum value is not given as a discreate value because we are dealing with statistically averaged atomic condition and some physical model of pressure ionization sis required for modeling of this problem. A model of the pressure ionization to SHM has been studied in [9], where it is modeled by decreasing the number of states in the upper bound levels.

$$g_n = \frac{2n^2}{1 + \left(a\frac{r_n}{R_0}\right)^b} \tag{8.27}$$

The fitting constants a and b have been chosen as a = 3 and b = 4 to correspond to Thomas-Fermi result [10]. In (8.23), the pressure ionization is determined by the



Fig. 8.12 (a) The charge state of aluminum as a function of temperature and density calculated by SHM for AIM. In high-temperature and low density, the ionization is due to thermal effect and shell structure is clearly seen. In the low temperature and high density, the pressure ionization increases the number of free electrons [6]. (b) The ionization potential of an isolated aluminum atom calculated with SHM (black dots). For comparison, the same data are also shown with precise method, Hartree-Fock calculation (triangles). Reprinted with permission from Ref. [6]. Copyright 1998 by Oxford University Press

electron orbit radius divided by the ion spere radius. It is intuitively reasonable that the bound state disappears abruptly for the electron orbit overlaps the orbits of nearby bound electrons.

In Fig. 8.12a, the charge Z^* as function of density and temperature is plotted for the case of aluminum (Z = 13) at high density plasma state [6, 9]. The shell structure is obtained for thermal ionization and pressure ionization is clear with increase of density. Note that the change of P_n , $-E_n$, and Z_n due to the temperature increase at density 0.1 g/cm³ in Fig. 8.12a is shown in [10] as well as the case of gold, where $n_{max} = 5$ and 10 are assumed for aluminum and gold, respectively.

In Fig. 8.12b, the ionization potential energy is also plotted without the pressure ionization effect, namely for an isolated aluminum atom. Energy jump due to shell structure of K-shell and L-shell is well reproduced by SHM (black dots) same as the result of Hartree-Fock calculation (triangles) [10].

8.3.3 Screened Hydrogen Model with (n, l)

The SHM has been extended to include angular momentum dependence in AIM. It is well-known that the degeneracy of the angular momentum quantum number ℓ at each principal quantum state *n* is accidental in case of hydrogen or hydrogen-like atom, where the potential is exactly proportional to 1/r. In the case of multi-electron

bound atom, binding energy of each ℓ -state in the same n-shell has different values and no degeneracy appears. So, depending on how precise atomic model is required, inclusion of n and ℓ in SHM is natural.

A self-consistent model based on a nonrelativistic screened-hydrogenic model (SHM) with ℓ -splitting has been developed to calculate the **equation of state (EOS)** of matter in local thermodynamic equilibrium [11]. This model takes account of the quantum subshell effect to go beyond the simple semiclassical and statistical Thomas-Fermi approach to obtain the electronic properties. The whole model is fast, robust, and reasonably accurate over a wide range of temperatures and densities. New screening constants are given in [11, 12]. In this case, the total energy of bound electrons is given in the same form as (8.17)

$$E_{ion} = -I_H \sum_{k} \left(\frac{Z_k}{n_k}\right)^2 \tag{8.28}$$

where $k = \{n, \ell\}$ and the energy sprit by ℓ is included in Z_k in the form same as (8.13).

$$Z_k = Z - \sum_j \sigma_{j,k} \left(1 - \frac{\delta_{jk}}{D_k} \right) P_j \tag{8.29}$$

where j also represents the configuration $j = \{n, \ell\}$ and the energy split by ℓ comes from the ℓ dependence of the set of the screening constant ($\sigma_{j, k}$) and the integer degeneracy of subshell k as follows.

$$D_k^0 = 2(2\ell_k + 1) \tag{8.30}$$

The screening constant $(\sigma_{j, k})$ are calculated by fitting over a large data basis containing nonrelativistic ionization potentials and excitation energies calculated using the Superstructure code and the multi-configuration Dirac–Fock code [12]. Note that additional assumption is also adopted in [11].

In [11], the fractional occupation number (P_k) is not given by Fermi-Dirac distribution, but it is calculated so that the electric Helmholtz free energy per average ion of the plasma (F_e) becomes minimum at fixed density and electron temperature.

$$F_e = F_{bound} + F_{free} + F_{ion-sphere} \tag{8.31}$$

In (8.31), F_{bound} is free energy of the average ion subsystem in the bound state given by SHM, F_{free} is the free energy of homogeneous free electron gas, and $F_{ion - sphere}$ is the contribution by the continuum lowering.

The free energy of the bound electrons is given with E_{ion} in (8.28) as

$$F_{bound} = E_{ion} - TS_{bound} \tag{8.32}$$

According to Boltzmann law on the entropy, S_{bound} is the sum of all bound state as

$$S_{bound} = -k_B \sum_{k} \left[P_k ln \left(\frac{P_k}{D_k} \right) + (D_k - P_k) ln \left(\frac{D_k - P_k}{D_k} \right) \right]$$
(8.33)

where the decrease of the number of states by pressure ionization effect given in (8.23) is also modeled and D_k is reduced from D_k^0 in (8.30).

It is too much to repeat the description in [11] and let us see the resultant **shock Hugoniot** relation with EOS derived by this SHM. The density jump of a single shock wave is plotted in Fig. 8.13 and compared to the present SHM, QEOS, and experimental data [11]. The QEOS is an EOS model widely used in laser plasma study [13] and the electron EOS is based on Thomas-Fermi model described in the next section. The QEOS is given by separating the total free energy as in (8.9) and the cold and ion components are given with so-called **Cowan model**.

In Fig. 8.13, EOS consisting of SHM for electron component and Cowan model for ion is shown as SHM-QEOS and the cases of three different coefficients of the ionization potential lowering given in (8.20) with different constants are plotted



Fig. 8.13 Shock Hugoniot data of aluminum from an experiment (*) and the present SHM with different coefficients and the original QEOS data. Reprint from Ref. [11]. Copyright 2012, with permission from Elsevier



Fig. 8.14 The maximum compression rate as a function of different atomic elements (nuclear charge). As seen in Fig. 8.13, all solids have the maximum compression rate characterized by the atomic shell structure. The present SHM results are compared to other theoretical data. Reprint from Ref. [11]. Copyright 2012, with permission from Elsevier

[11]. It is clear that all provides almost the same Hugoniot curve and the scattered experimental data are well explained. Just a qualitative difference is that QEOS does not give the shell effect of electron orbits, while the SHM predicts the effect.

The effect of shell in atom is emphasized or clearly observed in Fig. 8.14, where the maximum compression ratio is plotted for all atomic number Z [11]. All curves are theoretical prediction and the simple current SHM can reproduce the prediction with more complicated calculation by Johnson and Pain.

Let us consider that physics giving the oscillating structure in Figs. 8.13 and 8.14. In the case where the ionization happens in the shock surface region, a part of shock compression energy is used for ionization. This is regarded that the freedom of the thermodynamic system increased. As shown in Chap. 3, the density ration of strong shock wave is a function of the freedom of the gas, and the increase of the number of freedom N results the increase of compression ratio. The increase of the density ratio more than four (= $2.712 \times 4 = 10.8 \text{ g/cm}^3$) in Fig. 8.14 is due to this ionization effect. In the limit of the strong shock wave, the ratio reduced to the value of four, because the ionization energy is relatively small compared to the shock pressure work.

The periodic structure seen in Fig. 8.14 is also due to the ionization energy loss in the compression. The first peak is for Na (Z = 11), K (=19), and so on. They are transition metal with one electron in the outer shell. In the case when the shock is strong to ionized this electron, the high-density compression is observed.

8.4 Thomas Fermi Model for an Ion Sphere

To consider the physical property of compressed matters, a variety of theoretical models have been proposed to calculate the statistically averaged density distribution as consistently as possible. One of the convenient ways to calculate the electron density distribution for a system with a nucleus at the center and the surrounding electrons is **Thomas-Fermi (TF) model** as studied in early time of modern physics [14]. The TF model is still widely applied in many quantum systems, even to a hydrogen atom since it is very easy to solve numerically and provides approximate electron density profile in a compressed atom.

Although it is easy to solve computationally at the present, it is interesting to know that R. Feynman wrote how to do numerical calculation before the computer was invented [15]. About forty wives of scientists gather in a classroom and follow Feynman's instructions to turn the hand-cranked calculators, dividing the work among them and producing numerical values. He writes the results on the blackboard as the wives obtained in the numerical calculations. Although the TF model is not so complicated as seen below, it was difficult to solve without such human power before the computer era.

The basic equation to be solved is Poisson equation to the potential $\phi(r)$,

$$\varepsilon_0 \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \phi \right) = -Ze\delta(r) - en_e(r)$$
(8.34)

where $n_e(r)$ is the radial distribution of electron density around the nucleus with charge Z. It is assumed that the electron density is given by Fermi-Dirac statistics.

$$n_e(r) = \int \frac{2}{\hbar^3} f_{FD}(r, p) d^3 p = \frac{8\pi}{\hbar^3} \int_0^\infty p^2 f_{FD}(r, p) dp$$
(8.35)

where $f_{FD}(r, p)$ is the **Fermi-Dirac distribution**.

$$f_{FD}(r,p) = \frac{1}{1 + exp\left\{\frac{p^2/2m - e\phi - \mu}{T}\right\}}$$
(8.36)

It is clear that above equations are enough to determine the density profile $n_e(r)$, once the charge neutral sphere radius R_0 is given and the chemical potential is determined so that the charge neutrality is satisfied in the ion sphere. In the limit $(\mu \rightarrow -\infty)$, the electron density (8.35) tends to the **Boltzmann distribution** for a given electric potential ϕ . Due to this reason, the TF model is an extension of classical **Debye-Hueckel model** to Fermion gas. Boltzmann distribution cannot be used in the case of high-density plasma, and the simple **Debye shielding model** should be replaced by TF model.

8.4.1 Screened Electron Density Distribution

Introducing x and y defined as

$$x = \frac{p^2}{2mT}, \quad y = \frac{e\phi + \mu}{T} \tag{8.37}$$

The electron density (8.35) is given in more simple form:

$$n_e(r) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{x^{1/2}}{1 + exp(x-y)} dx$$
(8.38)

It is more convenient to solve (8.34) with assumption that the radial function of potential is given like

$$\phi(r) = \frac{Ze}{4\pi\varepsilon_0 r} Y(r) \tag{8.39}$$

Then, (8.34) can be reduced to the second order differential equation to Y(r).

In high-density plasmas, the ion-ion Coulomb coupling is strong and it is good approximation to introduce the ion sphere defined in (8.5) and set the boundary $R = R_0$ here. It is also assumed that the same amount of charge is filled by electrons to make charge neutral in the ion sphere. Then, the problem to solve (8.34) becomes an eigen-value problem to the boundary conditions:

$$Y(0) = 1,$$
 (8.40)

$$\frac{d}{dr}\phi(r=R_0)=0\tag{8.41}$$

Since we assumed the form (8.39), the first term on RHS in (8.34) disappears. After rewriting (8.34) to the equation to Y(r), we obtain a second order nonlinear differential equation to Y(r). It is recommended to solve the equation to Y(r) by integrating from both boundaries. Such numerical method is called **shooting method** and the eigen value μ starting with a trial value at the beginning should be converged to the value so that both solutions integrated from the center r = 0 and from the boundary $r = R_0$ continuously match at a given fixed matching point.

In Fig. 8.15, the electron radial density profile obtained by the TF model is shown for an isolated neutral argon atom, where R_0 is infinity. The resultant radial density distribution is compared to that obtained by the **Hartree method** described in Chap. 5. It is noted that the Hartree method solves Schrodinger equation to all wave functions for the bounded N electrons by including the Coulomb interaction. Although the exchange interaction is not included in this Hartree method, it is much better calculation than TF model. It is seen in Fig. 8.15 that electron density distribution obtained by such simple TF model is good enough in this case compared to that obtained by the Hartree method. Big difference is that the Hartree method can



Fig. 8.15 The electron density radial distribution of isolated neutral argon atom obtained by Thomas-Fermi model and more precise Hartree method. Since the Hartree method solve the wave functions and the shell structures are seen

include the effect of shell structure by filling states with different principal quantum numbers. TF cannot reproduce such quantum shell effect.

In the present TF model in high density and/or high temperature, it may be possible to divide the electrons into the bound and free components. There are two ways for the definition of the fraction of free electron component in the ion sphere as follows.

$$f_{free} = \frac{4\pi}{Z} \int_0^{R_0} n_e \left(\frac{p^2}{2m} - e\phi(r) \ge 0\right) r^2 dr$$
(8.42)

$$f_{free} = \frac{4\pi}{3Z} R_0^3 n_e(R_0)$$
(8.43)

The first one (8.42) is the case regarding the electrons with positive energy are the free electron, while the second one (8.43) simply regards the free electron density is equal to the density at the boundary of the ion sphere.

8.4.2 Fitting Formula of TF Results

Many scientists have developed approximate fitting formulae for the numerical result of Thomas-Fermi model. One of the best is the formula derived by R. M. More [4] to be shown here. This can be applied any materials with different atomic and charge numbers. As mentioned by More, Thomas-Fermi equation has a kind of self-similarity to the hydrogen case (Z = 1 and A = 1). It is well-know that Thomas-Fermi data such as electron pressures P_e, and internal energy ε_e of plasma with Z and A can be reproduced once we have the data of the hydrogen case. At first, the plasma

density and electron temperature should be converted to the equivalent physical quantities for the hydrogen plasma.

$$\rho_1 = \frac{\rho}{AZ}, \quad T_1 = \frac{T}{Z^{4/3}}$$
(8.44)

More has shown that the charge state of any material at any density and temperature obtained with the numerical result of TF model can be reproduced by the following fitting formula.

$$Z^*(\rho, T) = Z \frac{x}{1 + x + \sqrt{1 + 2x}}$$
(8.45)

where x is a function of (ρ_1, T_1) [4].

Inserting this x into (8.45), the effective charge predicted by TF model is very precisely given. The resultant of effective ionization charge for Z = 1 and A = 1 is shown in Fig. 8.16. The density and temperature correspond to ρ_1 and T_1 and it is easy to obtain the charge state with the relation (8.44) for any elements.

It is clearly seen in Fig. 8.16 that for a given density and/or temperature, the ionization increases with the temperature and/or density, respectively. The former tendency is thermal ionization and common even in low density plasma, while the



Fig. 8.16 Thomas-Fermi model has self-similarity solution, and all data of different Z number can be produced with use of the solution for hydrogen. Figure shows the ionization charge as a function of density and temperature by use of the fitting formula (8.45)

latter is typical for the high-density plasma. Since the number of states for the bound state decreases with the increase of density, many electrons must be in the free state. This indicate that Fermi energy of the electrons increases with the density and the plasma becomes Fermi degenerate state. So, in the dense plasma with low temperature and high density, Fermi degeneracy of electrons becomes important.

8.4.3 Property of Thomas-Fermi Results

The effective charge Z* increases with the increase of density even at T = 0. Such ionization is called **pressure ionization**, because high density means the distance of nearby two ions makes a joint potential as schematically shown with the solid line in Fig. 8.17, and the **ionization potential depression (IPD) (lowering)** (χ) due to the overlapping of Coulomb potential allows the bound electrons in the higher-energy levels to be free. The pressure ionization is due to the depression of the ionization energy level by overlapping the potential of the nearby ions.

This has a very important information, since the depression of the ionization energy level means most of the upper-bounded discreet energy states with a large principal number should be eliminated in the partition function of (5.5). In solving the **Saha equation** of (5.14), most difficult point is the evaluation of the function of u_{ζ} and $u_{\zeta + 1}$. These values change dramatically depending on how the maximum quantum state can be regarded to be the bound states, since the number of states dramatically increases in the upper state as a single atom.

However, the physics image will change in the case of finite temperature, where the ions are moving due to thermal motion. In such case, it is better to obtain the probability for the nearest neighbor two ions. This is a problem of statistical physics, and it is informative to see the case of **Debye potential** for the ideal plasma. The

Fig. 8.17 The image of pressure ionization is shown by overlapping the potential profile of two isolated ions (dotted lines) and the potential by summing both (solid lines). The decrease of interatomic distance by imposed high pressure depresses the ionization energy level as the solid line



probability of another ion comes to the radius r of the central ion is given by the following Boltzmann distribution

$$f(r) = e^{-\frac{Ze}{T}\phi(r)} = exp\left(-\frac{Z^2e^2}{4\pi\epsilon_0 Tr}e^{-k_D r}\right)$$
(8.46)

Let us introduce the two dimensionless values.

$$\Gamma_{ii} = \frac{Z^2 e^2}{4\pi\varepsilon_0 T R_0} \tag{8.47}$$

$$x = \frac{r}{R_0} \tag{8.48}$$

where Γ_{ii} is called **ion-ion coupling parameter** and R_0 is the ion-sphere radius. Then, (8.46) is rewritten as,

$$f(x) = exp\left(-\frac{\Gamma_{ii}}{x}e^{-\frac{R_0}{\lambda_D}x}\right)$$
(8.49)

The condition of the ideal plasma requires the parameter Γ_{ii} is much smaller than unity. It is useful to see the radial structure of this probability. It is clear from (8.49) that f(x) tends to zero near r = 0 and two ions repel each other via Coulomb repulsive force. At far distant point f(x) = 1 and this function is monotonically increase with the radius. It is very reasonable and coincides with our intuitive image.

Most of bound electrons with orbit radius more than R_0 as an isolated atom will be continuum in such many-body system. In case of hydrogen, the average orbit r_n of a s-state wave function is given in (5.26).

$$r_n = a_B \frac{n^2}{Z} \tag{8.50}$$

It is easy to calculate the critical ion density whose orbit radius of the principal quantum state n satisfies the condition.

$$\frac{4\pi}{3}r_n^3 n_i = 1 \quad \to \quad n_i = 3 \times 10^{22} \frac{Z^3}{n^6} \left[1/cm^3 \right]$$
(8.51)

This approximately gives the critical principle number for pressure ionization. It is written also for hydrogen as

$$\rho_n = 0.05 \frac{1}{n^6} \quad \left[g/cm^3 \right] \tag{8.52}$$

At high-density plasma, such lowering is very essential.

At the same time, the number of states of free electrons is also decreases as increase of density. It is useful to know that the number of free electron states per unit volume is given to be

$$N(E) = 2 \int_0^E g(k) dk = \frac{1}{3\pi} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{3/2}$$
(8.53)

where N(E) is the number of states of free electron to the energy of E. It should be noted that the energy obtained by setting $N = Zn_i$ is **Fermi energy**. The number of free electron states per ion is also decrease in proportion to the inverse of ion density for a given energy E. This means that increase of density, the pressure ionization decreases the number of bound electrons, while the number of states of free electrons also decreases with the increase of density. Then, the required pressure of compression will increase due to Fermi degeneracy of free electrons.

It is noted that TF model would be good enough for many problems even for contemporary subjects. The potential profile obtained by TF model can be used for an approximate potential for one electron Schrodinger equation. If you calculate the electron energy-states in the TF potential, it approximately reproduces the electron shell-structure (1s, 2s, 2p, 3s, 3p but then 4s comes before 3d. . .) of the periodic table of Mendeleev chart. It also correctly predicts how that structure is changed for high-charge ions.

TF is simple because it is one equation for all the electrons. The more accurate methods (Hartree or Hartree-Fock) have a separate differential equation for each electron, so it is 26 equations for Fe. Actually, of course, only 13 because the two spins (up and down spin) have almost the same potential, same equation.

Historically, the TF model has been extended to include another physical effect as shown in Chap. 6 in Ref. [16]. For example, the extension to molecules such as a hydrogen bonding shown in Fig. 8.2. The attractive force by the exchange interaction has been included as Thomas-Fermi-Dirac model, where the exchange potential is modeled as a function of local density. The density divergence near the central nuclear charge has been eliminated by Thomas-Fermi-Dirac-Weizsacker model. These models have been developed before commonly use of the computer, but it is informative to know how quantum mechanical equation should be simplified by use of such models. As the progress of computing, the following direct calculation of multi-electron and many-body system has become more popular.

8.5 Density Functional Theory for Multi-electron Interacting System

We have studied the structure of atoms by assuming the ion sphere model. The electron density distribution or the wave function of each electron have been solved based on simple models derived from quantum mechanics. In the case of high-

density plasma, it is essential to consider the statistical properties of many electrons whose wavefunctions spread over many nuclei. The nuclei also move slowly by the Coulomb force due to neighboring ions and surrounding electrons. It is natural to study such system with many charged particles by solving so-called "*ab-initio*" problem. The *ab-initio* calculation means to solve the many-body problem quantum-mechanically as exact as possible by starting from multi-electron Schrodinger or Dirac equations, for example, the **Hartree-Fock** (**HF**) **equation** mentioned in Chap. 5 gives us the exact solution of the grand state of the many-electron system [16, 17]. To solve HF equation directly, however, faces numerical difficulty even with the supercomputer, and the **density functional theory** (**DFT**) based on the HF theory is widely used for the *ab-initio* calculation.

The rapid progress of supercomputer has made it possible to solve such complicated problem in a reasonable CPU time. As shown in Fig. 8.1, it is surprising to know the progress of CPU time, for example, from the fastest supercomputer in the world *Earth simulator* in 2002 to now *Fugaku* in 2020 [18]. Their speeds are respectively 40 TF and 400 PF, namely 10,000 times progress in CPU over the last 18 years in Japan (the world). Computer scientists are always demanded to challenge new and more *ab-initio* methods according to the progress of computer capability.

Note, however, that if we would like to solve the N electron system with M classical nuclei like fixed points in space, Schrodinger equation for N electron system becomes a problem to solve it in 3N space dimension in three-dimensional real space, for example, in HF theory. Of course, challenges to solve HF equation by integrating over 3N space by use of Monte Carlo method has been carried out like a **quantum Monte Carlo (QMC)** [19].

More flexible numerical method, on the other hand, has been widely used mainly in the solid-state physics. In this method, Schrodinger equation for N electrons is independently solved as one-electron problem in an effective potential given as a function of the local electron density. This is called **density functional theory** (**DFT**), which results from the work of Hohenberg, Kohn and Sham [16]. This method has been applied also to atoms and molecules. In laser-produced warm dense plasmas, DFT has been extended to the system with finite temperature, for example, as reviewed in [20].

The simulation codes of DFT have been developed with different numerical schemes. They have been compared as code-comparison for the case of solids at T = 0 in [21]. It is surprising to know that many codes gave almost the same results with good accuracy. Here, after a brief explanation of the Hartree-Fock theory, the basic equation of DFT is derived for the case of finite temperature.

8.5.1 Hartree-Fock Theory of Multi-electron System

In Sect. 5.3, how to study the quantum state of single atom with multi electrons has been discussed. In the case of Helium atom, anti-symmetry of the total electron wave function is required to provide not only Coulomb interaction but also the exchange

interaction between two electrons. When a system has N_n nuclei and N electrons, the total Hamiltonian of the system is given in the form for **Born-Oppenheimer** approximation, where nuclei are fixed.

$$H_H = \sum_{i=1}^{N} H_{H,i}$$
(8.54)

where $H_{H,i}$ is one-electron Hamiltonian indicated with "*i*" for the case when the wave functions of the other electrons are given.

$$H_{H,i} = -\frac{\hbar^2}{2m} (\nabla_i)^2 - \frac{e^2}{4\pi\varepsilon_0} \sum_{k=1}^{N_n} \frac{Z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \frac{e^2}{4\pi\varepsilon_0} \sum_{j\neq i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} |\psi_j|^2 \qquad (8.55)$$

Assume the total wave function Ψ is given as the product of single electron, namely, Ψ has the form.

$$\Psi_H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\cdots\cdots\psi_N(\mathbf{r}_N)$$
(8.56)

This assumption is called the **Hartree approximation**. Note that the subscripts of the wave functions are independent number of the subscripts of the positions. The Schrodinger equation for $\psi_i(\mathbf{r}_i)$ is shown as

$$H_{H,i}\psi_i(\mathbf{r}_i) = \varepsilon_i\psi_i(\mathbf{r}_i) \quad \text{for } i = 1, \dots N$$
(8.57)

where ε_i is the eigen value of the i-th electron and Coulomb interaction energy with the other electrons is consistently included. Since (8.57) is a nonlinear equation and is required to be solved iteratively by a numerical method so that the numerical solution is self-consistent. The solution of (8.57) has no exchange interaction between the electrons. The formulation should take account of the property of Fermion of the electron.

It is known that the total wave function of the Fermion gas should be antisymmetry. Namely, the exchange of two electrons in the system should change the sign of the total wave function. A simple form of (8.56) is not acceptable as Fermion gas. The anti-symmetric total wave function is given by the following Slater determinant. It also should include the freedom of the electron spin, up or down (denoted with "s"). For simplicity, the coordinate including the spin (**r**, s) is shown as **x** in what follows.

$$\Psi_{HF}(\boldsymbol{x}_1, \boldsymbol{x}_2, \dots, \boldsymbol{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\boldsymbol{x}_1) & \cdots & \psi_N(\boldsymbol{x}_1) \\ \vdots & \ddots & \vdots \\ \psi_1(\boldsymbol{x}_N) & \cdots & \psi_N(\boldsymbol{x}_N) \end{vmatrix}$$
(8.58)

This is called **Hartree-Fock approximation**. Then, the Schrodinger equation for the i-th electron is given as the same form, but the Hamiltonian becomes differential and integral operator \mathcal{F} [16].

$$E_{HF} = \langle \Psi_{HF} | H | \Psi_{HF} \rangle = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left(J_{ij} - K_{ij} \right)$$
(8.59)

where H_{i} , J_{ij} , and K_{ij} are defined as

$$H_i = \int \psi_i^*(\boldsymbol{x}) \left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0} \sum_{k=1}^{N_n} \frac{Z_k}{|\boldsymbol{r} - \boldsymbol{R}_k|} \right] \psi_i(\boldsymbol{x}) d\boldsymbol{x}$$
(8.60)

$$J_{ij} = \frac{e^2}{4\pi\varepsilon_0} \iint |\psi_i(\mathbf{x_1})|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_j(\mathbf{x_2})|^2 d\mathbf{x}_1 d\mathbf{x}_2$$
(8.61)

$$K_{ij} = \frac{e^2}{4\pi\varepsilon_0} \iint \psi_i^*(\mathbf{x}_1)\psi_j(\mathbf{x}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_j^*(\mathbf{x}_2)\psi_i(\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}$$
(8.62)

Note that all integrals result real values and $J_{ij} \ge K_{ij} \ge 0$. The J_{ij} is **Coulomb integral** representing the Coulomb repulsive force between all two electrons in the system. On the other hand, the K_{ij} is the **exchange integral** and stems from the force due to the exclusive principle of Fermion particles. The exchange energy is purely quantum mechanical one and it appears because we have adopted the total wave function in the form Slater determinant to guarantee its anti-symmetry. It is important to note the fact that both energies look unphysical interaction for the case of j = i, while this unphysical case is excluded for the total energy in (8.59) since

$$J_{ii} = K_{ii} \tag{8.63}$$

We adopt (8.63) for extending to the density functional formulation to be discussed soon.

Same as the Hartree approximation, we must adopt the wave functions $\psi_i(\mathbf{r})$ orthogonal, and then the following N coupled Schrödinger equation is obtained for the i-th single wave function.

$$\widehat{\mathcal{F}}(\boldsymbol{x})\boldsymbol{\psi}_i(\boldsymbol{x}) = \sum_{j=1}^N \varepsilon_{ij}\boldsymbol{\psi}_j(\boldsymbol{x})$$
(8.64)

where $\widehat{\mathcal{F}}$ is **Hartree-Fock Hamiltonian**.

$$\widehat{\mathcal{F}}(\boldsymbol{x}) = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0} \sum_{k=1}^{N_n} \frac{Z_k}{|\boldsymbol{r} - \boldsymbol{R}_k|} + \widehat{g}(\boldsymbol{x})$$
(8.65)

In (8.64), ε_{ij} is the eigen-value derived in matrix. (8.64) is called **Hartree-Fock** equation.

On the right-hand side of (8.65), the first term the kinetic energy, the second term is Coulomb interaction with all nuclei, and the third term is integral operator due to the Coulomb and exchange interaction of the i-th electron with all other electrons in the system. It is given in the form.

$$\widehat{g}(\mathbf{x}) = \widehat{j}(\mathbf{x}) - \widehat{k}(\mathbf{x})$$
 (8.66)

where the Coulomb coupling operator and exchange interaction operator are given to be

$$\widehat{j}(\boldsymbol{x})\psi_{i}(\boldsymbol{x}) = \frac{e^{2}}{4\pi\varepsilon_{0}}\sum_{j=1}^{N}\int\left|\psi_{j}(\boldsymbol{x}')\right|^{2}\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\psi_{i}(\boldsymbol{x})d\boldsymbol{x}'$$
(8.67)

$$\widehat{k}(\boldsymbol{x})\psi_{i}(\boldsymbol{x}) = \frac{e^{2}}{4\pi\varepsilon_{0}} \sum_{j=1}^{N} \int \psi_{j}^{*}(\boldsymbol{x}')\psi_{i}(\boldsymbol{x}') \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\psi_{j}(\boldsymbol{x})d\boldsymbol{x}'$$
(8.68)

A new eigen value ε_i defined as follows is obtained by integrating (8.65) after the product with ψ_i^* .

$$\varepsilon_{i} \equiv \varepsilon_{ii} = \left\langle \psi_{i} | \widehat{\mathcal{F}} | \psi_{i} \right\rangle = H_{i} + \sum_{j=1}^{N} \left(J_{ij} - K_{ij} \right)$$
(8.69)

Then, the total energy is given as

$$E_{HF} = \sum_{i=1}^{N} \varepsilon_i - V_{ee} \tag{8.70}$$

$$V_{ee} = \frac{1}{2} \sum_{i,j=1}^{N} \left(J_{ij} - K_{ij} \right)$$
(8.71)

It is easily verified that the total wave function given in Slater determinant results the following form for two location probability after integration by $x_3, \dots x_n$ space.

$$\mathbf{n}(\boldsymbol{x}_1, \boldsymbol{x}_2) = \frac{1}{N(N-1)} \sum_{k,l}^{N} |\psi_k(\boldsymbol{x}_1)|^2 |\psi_l(\boldsymbol{x}_2)|^2 - \psi_k^*(\boldsymbol{x}_1) \psi_k(\boldsymbol{x}_2) \psi_l^*(\boldsymbol{x}_2) \psi_l(\boldsymbol{x}_1) \quad (8.72)$$

The probability of two electrons at the same place and with the same spin $x_1 = x_2$ becomes null.

8.5.2 Kohn-Sham Density Functional Theory (DFT)

Kohn-Sham theory provides the exact solution for the grand state of the system with many electrons and many nuclei by solving the following eigen-value problem of each electron. Then, the exchange effect due to the spin is modeled in the effective potential as a function of density. It starts to solve the single electron Schrödinger equation with the effective Hamiltonian derived by Kohn-Sham, $H_{KS}(\mathbf{r})$.

$$H_{KS}(\mathbf{r})\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}) \tag{8.73}$$

where Kohn-Sham Hamiltonian is given in the form

$$H_{KS}(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\boldsymbol{r})$$
(8.74)

On RHS in (8.74), the first term is the kinetic energy of electron and the second term is the effective potential which is only the function of the electron density defined by

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$
(8.75)

It is assumed that KS potential is given as a function of density

$$V_{KS}(\mathbf{r}) = f[n(\mathbf{r})] \tag{8.76}$$

It is important to note that the effective potential (Kohn-Sham) potential $V_{KS}(\mathbf{r})$ is common to all N electrons, so the eigen-energy ε_i and eigen-function $\varphi_i(\mathbf{r})$ can be obtained by solving (8.73) as a single electron system. The orthogonality of all wave functions is certified. In solid-state physics, it is enough to obtain the N electron configuration after solving (8.73) for N wave functions from the lowest energy state. However, in the case of dense plasmas, it is required to solve many wave functions including excited states because of thermal excitation of electrons.

For the case where the computational system is assumed to have N_n nuclei and N electrons, the KS potential is given in the form:

$$V_{KS}(\mathbf{r}) = V_{ne}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})$$
(8.77)

where $V_{ne}(\mathbf{r})$ is Coulomb potential to the i-th electron by the nuclei and given as

$$V_{ne}(\mathbf{r}) = -\frac{e^2}{4\pi\varepsilon_0} \sum_{j=1}^{N_n} \frac{Z_j}{|\mathbf{r} - \mathbf{R}_j|}$$
(8.78)

where Z_j and R_j are the nuclear charge and position of the j-th nucleus. The second term on RHS in (8.77) is the **Hartree potential** by all electron at the point *r*.

$$V_H(\mathbf{r}) = \frac{e^2}{4\pi\varepsilon_0} \int d^3\mathbf{r}' \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}$$
(8.79)

The third term in (8.77) stands for the potential giving the force stemming from the **exchange and correlation (xc) energy** among N electrons. In DFT, both energies are represented with E_{xc} as a function of only the electron density $n(\mathbf{r})$. Then, $V_{xc}(\mathbf{r})$ in (8.77) is defined by the functional derivative.

$$V_{xc} = \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \tag{8.80}$$

It is better to say that if the exchange-correlation (xc) energy E_{xc} is derived as a function of the local density exactly, Kohn-Sham density functional theory is exact. This exchange-correlation energy E_{xc} is not only these two energies, but it represents all energy left in (8.77) stemming from multi-electron system. It is hard job to correctly formulate the **xc energy**, and it is usually defined approximately.

In solving DFT with computers, many numerical schemes have been developed. This is reported as code comparison in [21]. Typical numerical issue in calculating all wave functions with (8.73) appear from the fact that some electron wave function changes smoothly far from any nuclei, while it changes rapidly near a nucleus due to the deep Coulomb potential.

8.5.3 Density Functional Theory for Finite Temperature System

The Kohn-Sham theory has been applied to the case of solids, where total electrons are in the ground state. In the case of finite electron temperature (T \neq 0), we must extend the Kohn-Sham theory so that the electrons are excited thermally to have a finite probability at the higher energy levels. Then, it is reasonable to assume that the electron energy distribution is given by Fermi-Dirac distribution f_{FD} .

$$f_{FD}(\varepsilon_i) = \frac{1}{exp[(\varepsilon_i - \mu)/T]}$$
(8.81)

where μ is the chemical potential. With the factor two of spin freedom, the electron density is given as

$$n(\mathbf{r}) = 2\sum_{i=1}^{N} f_{FD}(\varepsilon_i) |\varphi_i(\mathbf{r})|^2$$
(8.82)

The unknown chemical potential μ is determined to satisfy the electron number conservation relation:

$$N = 2\sum_{i=1}^{N} f_{FD}(\varepsilon_i)$$
(8.83)

After solving the above relations with one-electron Schrödinger Eq. (8.73) iteratively, the self-consistent density and each eigen-energy give the total energy of the electrons E in the system.

$$E = \sum_{i=1}^{N} f_{FD}(\varepsilon_i)\varepsilon_i - \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}$$
$$- \int d^3 \mathbf{r} V_{xc}(\mathbf{r})n(\mathbf{r})$$
(8.84)

where the first term is the sum of eigen energies of N electrons as single electron. Since this term double counts the Coulomb interaction energy among multielectrons, the second term is needed in (8.84).

In (8.84), the total exchange energy for each electron is defined by the following integral.

$$E_{xc} = \int d^3 \boldsymbol{r} \varepsilon_{xc}(\boldsymbol{r}) n(\boldsymbol{r})$$
(8.85)

It is very hard subject to derive the local exchange-correlation energy $\varepsilon_{xc}(\mathbf{r})$ as a function of the local density $n(\mathbf{r})$ [22]. In the form (8.84), the xc energy is also double counted and the fourth term is required.

In the actual computation, the coupled equations are solved iteratively so that the numerical result becomes self-consistent.

In [20], density functional theory with molecular dynamics (DFT-MD) has been developed to solve the problem including the ion motion. New formulation of the xc energy for finite-temperature hydrogen has been derived and its effect has been discussed in WDM. Using the Kohn-Sham approach, the xc energy of the system, $\epsilon_{xc}(\mathbf{r})$, is replaced by the xc free energy $f_{xc}(\mathbf{r})$ within the local density approximation (LDA) based on parametrized path integral Monte Carlo data for the **uniform electron gas (UDG)** at warm dense matter conditions [20].

In the UDG, Slater has derived the following simplest form of the xc energy as a function of density for solids [16]:

$$\varepsilon_{xc}(\mathbf{r}) = an^{1/3}, \qquad a = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3}$$
 (8.86)



Fig. 8.18 The density surface distribution for given density in three different stage in laser compression of solid aluminum. The simulation is carried out with time-dependent density functional theory (TDDFT). Reprinted by permission from Macmillan Publisher Ltd: ref. [23], Copyright 1993

This simplest form has been used for many cases. The intensive works have focused on the improvement of the density functional form of the xc energy as general form for the grand state in solids. In the case of WDM system with finite temperature, the research to formulate the xc energy is still challenging subject [22].

In Fig. 8.18, three snap shots of time-dependent density functional theory simulations of the formation of WDM are shown This is the result of TDDFM based on DFT-MD to the following experiment [23].

Two 4.5 J laser beams were used to irradiate 50-µm-thick Al foils (initial density of $\rho = 2.7$ g/cm³) coated with 2-µm-thick perylene. The laser beams were absorbed by the perylene, heating the material, and two counter-propagating multi-Mbar shock waves were launched into the solid aluminum by ablation pressure. Within 0.5 ns, the laser power rose to a power that was constant over time, with an intensity of 35 TWcm⁻². Each laser operated at 527 nm and was spatially smoothed over a focal spot of 60 µm to launch strong shocks.

The left is solid state, the middle is melting phase, and the right is WDM state. In the figure, the ions (blue) abandon their lattice positions. Although core electrons (grey) remain mostly unchanged, the delocalized conduction electrons (represented by orange iso-surfaces) are disturbed from the very regular structure in the lattice.

8.5.4 Time Dependent DFT

Numerical method, of course, changes in solving the **time dependent DFT** (**TDDFT**). The basic equation to be solved is now the following **time-dependent** Schrodinger equation.

$$i\frac{\partial}{\partial t}\varphi_i(\boldsymbol{r},t) = H_{KS}(\boldsymbol{r},t)\varphi_i(\boldsymbol{r},t)$$
(8.87)

The Kohn-Sham Hamiltonian is given with the same form (8.74) as functions of the time-dependent density $n(\mathbf{r}, t)$. The density is defined by (8.82). If we use the finite dereference method to the time integration, the iteration should be carried out to keep the consistency of Kohn-Sham theory at each time step.

At first, consider that case of very fast phenomena seen when an ultra-short laser pulse irradiate gas with atom or molecule. Even in such a case of single atom or molecule, DFT is useful to obtain the spectrum of **higher-harmonic generation** (**HHG**) due to nonlinear oscillation of electrons in the gas. In Chap. 2 (Volume-1), the **multi-photon ionization** process has been discussed. When an intense laser is irradiated with the intensity less than dominant ionization process, the bound electrons oscillate in the potential by nuclei and this un-harmonic oscillation causes the emission of many harmonic radiations.

As shown in [24], the time dependent potential by the laser electric field $V_L(\mathbf{r}, t)$ is given under the dipole approximation.

$$V_{KS}(\mathbf{r}) \Rightarrow V_{KS}(\mathbf{r}, t) + V_L(\mathbf{r}, t)$$
(8.88)

where

$$V_L = E_0 f(t) \sin(\omega t) \boldsymbol{r} \cdot \boldsymbol{\alpha} \tag{8.89}$$

where the peek electric field is E_0 and the structure of laser envelope is f_0 and α is the unit vector showing the laser polarization. Note that (8.87) is applicable only in the non-relativistic case. In the ultra-intense and relativistic laser case, Schrödinger equation should be replaced by Dirac equation and the potential V_L should include the force by magnetic field of laser.

It is useful to see TDDFT simulation applied for the HHG from the He atom as shown in Fig. 8.19 [24]. Note that the solid line is obtained from the simulation and the squares represent experimental data. It is concluded that even atomic or molecular gas system, DFT results reasonable HHG spectrum being able to explain the corresponding experiment.

More complicated case where laser is irradiated to solid and other has been carried out. The time-dependent simulation code is now available as an open source (name SALMON) in our community [25].

8.5.5 Quantum Molecular Dynamics (QMD)

To study a long-time evolution of WDM, it is necessary to solve the motion of nuclei consistently. It is reasonable to assume that since the mobility of electrons is much



Fig. 8.19 The higher-harmonic generation (HHG) is clearly seen by the post process of the dipole moment spectral analysis with total wave functions obtained from TDDFT. Reprinted with permission from Ref. [24]. Copyright by Annual Review Journal

larger than that of nuclei, DFT is applicable to given positions of nuclei at each time step. The motion of a nucleus k is governed by the following equation of motion.

$$M_k \frac{d}{dt} \boldsymbol{v}_k = -\nabla_k [E_e(\boldsymbol{R}_k) + V(\boldsymbol{R}_k)]$$
(8.90)

where M_k , v_k , and R_k are the mass, velocity, and position of a nucleus k. $E_e(R_k)$ is the total electron energy at the point R_k calculated by DFT for electron system. In addition, the nucleus k is affected the Coulomb force by the other nuclei whose potential energy is given as

$$V(\boldsymbol{R}_k) = \frac{e^2}{4\pi\varepsilon_0} \sum_{j=1}^{N_n} \frac{Z_k Z_j}{|\boldsymbol{R}_k - \boldsymbol{R}_j|}$$
(8.91)

Since the force to nuclei is given at each time step by quantum mechanical method DFT, it is QMD and different from the classical molecular dynamics (MD) where usually the force is given by Lenard-Johns type potential shown in (8.4).

In Fig. 8.19, three snap shots of time dependent DFT simulation are already shown [23]. This is the case of DFT-QMD simulation. Do not confuse that TDDFT for (8.87) is the time-dependent simulation of electron dynamics for fixed nuclei and the time step is very short, while the DFT-QMD is the time evolution of ion motions with time step much longer than the previous case. It is, of course, easy to extend TDDFT to follow the motion of nuclei, but the problem is the time-consuming computation time.

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