CHAPTER 4

INTERMOLECULAR POTENTIALS

In MD simulations of physical systems, all of the information earned in the final stage relies upon potential functions describing the interactions among particles in the system. The functional form varies accord to the characteristics of components, such as the electromagnetic force, overlap, induction, etc. However, the potential of any system can be written, in general form, as

$$U(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_n)=\sum_{i=1}^{n}U_1(\vec{r}_i)+\sum_{i=1}^{n}\sum_{j=i+1}^{n}U_2(\vec{r}_i,\vec{r}_j)+\sum_{i=1}^{n}\sum_{j=i+1}^{n}\sum_{k=j+1}^{n}U_3(\vec{r}_i,\vec{r}_j,\vec{r}_k)+\ldots \qquad (4.1)$$

The first term of the right side of equation, $U_1(\vec{r}_i)$, represents the influence from a potential due to the external force field, such as the gravity field. The second function, $U_2(\vec{r}_i,\vec{r}_j)$, called the pair potential, represents the potential from two body interactions. It is usually the most important term and can be written as a function of the magnitude of the distance between the pairs. The next term, $U_3(\vec{r}_i,\vec{r}_j,\vec{r}_k)$, called the three-body term, is generally expected to be small and is neglected in a number of models because it slows down computer simulations as well as requiring much time and effort for the development of the function. However, in the case of condensed systems, the three-body term probably becomes meaningful and affects some outrun properties. The remaining terms, called non-additive or many-body interaction terms, are generally expected to have very small effects on the system.

4.1 Pair Potential

As the simulated system for this study is a quantum system consisting of metal ions and free electrons in liquid ammonia, the system has to be described by the pair potential, three-body ammonia-metal-ammonia potential, and pseudopotential. The last one is necessary to describe the effect of the free electrons on the pair which are routinely used for classical simulations. Therefore, in the next sections, the three types of functions are described.

The direct procedure to obtain the pair potentials in analytical form may be written in a sequential series of steps:

- Select a reliable basis set for the SCF calculations. Various basis sets are tried. One that minimizes the BSSE and interaction energy will be selected. However, the computer time consumed in SCF calculations is also a concern.
- Perform the SCF calculations for various configurations of the Ca(II)-ammonia system to obtain the interaction energy

  $$\Delta E_{pair}^{SCF} = E[LM] - E[L] - E[M], \tag{4.2}$$

  where M and L denote the calcium ion and the ammonia molecule, respectively.
- Fit the computed binding energy to analytic functions. Many functional forms, such as

  $$\Delta E(r_{ij}) = \sum_{ij} \frac{a_{ij}}{r_{ij}^{n}} + \frac{b_{ij}}{r_{ij}^{m}} + \frac{q_i q_j}{r_{ij}}, \tag{4.3}$$

  where m = 2, ..., 6, n = 8, ..., 15, or

  $$\Delta E(r_{ij}) = \sum_{ij} \frac{a_{ij}}{r_{ij}^{n}} + b_{ij} \exp(-c_{ij} r_{ij}) + \frac{q_i q_j}{r_{ij}} \tag{4.4}$$

are tested.

- Compare the quality of tested functions. The quality depends on how close the values calculated by the fitting function is to the value from SCF. However, it is also important that the minimum points from both SCF calculations and the fitting function are close together.

4.2 Three-Body Correction

It has been known since the early 1940s that many-body effects can have an important influence on the results obtained from the computer simulations. This can lead to a serious modification of the simulation models, especially in cases of condensed-phase systems [Elrod and Saykally 1994]. In 1962, in order to simplify the calculation of many-body exchange effects, Jansen [1962] introduced the Gaussian effective electron model and found that first-order three-body exchange effects for the rare gases could be as large as 20% of the two-body exchange energies. Furthermore, Lombardi and Jansen [1968] also extended the approach to four-body interactions and found that these effects were negligible for most geometries of interest. These observations have been illustrated for a monatomic gas system [Polymeropoulos and Brickmann 1982] and numerous cases of ions in aqueous solution [Kim et al. 1995; Lybrand and Kollman 1985; Kelterbaum et al. 1994; Dang 1992]. In addition, recent studies of Na(I), Mg(II), or Zn(II) solvation in liquid ammonia by Monte Carlo simulations showed that the three-body corrections reduce their first shell coordination number from 9 to 8, 10 to 6, or 9 to 6, respectively [Hannongbua 1997; Hannongbua, Kerdcharoen and Rode 1992].

In this dissertation the role of three-body interactions on the structural and dynamical properties of the solution has been investigated. The presence of three-body corrections leads to the reduction of the first shell coordination number of Ca(II) in liquid ammonia from 9 to 8, the increase of the size of the solvation shell by 0.33 Å and the disappearance of the second solvation shell.

4.3 Pseudopotential Method

In the following subsections, the pseudopotential method will be reviewed, as well as the important approximations. We shall also see how this method relates to the interatomic interactions in the system of particles with free electrons. The form factors and dielectric functions employed in this work are shown in the last subsections.

In the pseudopotential method there are 3 necessary assumptions.

i) The potential seen by each electron is, approximately, an average of the actual interactions, called a self-consistent potential. These potentials depend only on which states are occupied by electrons.

ii) The energy levels are categorized into core and conduction-band states. The core states are treated as localized, and the wave functions are the same as in the isolated ions. The others, the valence electrons, are treated as in conduction-band states.

iii) Perturbation theory is used as the basis for computing the conduction-band states.

4.3.1 The orthogonalized plane wave

Let V(r) be the potential seen by each electron. We can write down the Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\varphi_i = E_i\varphi_i, \qquad (4.5)$$

where i is the index for the ith state. To distinguish between core and conduction-band states, the index α is substituted for core states and $\vec{k}$ for conduction-band states.

Suppose that all core states are known (assumption ii), and conduction-band states can be obtained from linear combinations of plane waves, which each must be orthogonal to the core states. Sets of these plane waves have been called orthorgonalized plane waves (OPW). An OPW of wavenumber $\vec{k}$ can be written

$$\left|\vec{k}\right\rangle_{OPW} = \left|\vec{k}\right\rangle - \sum_{\alpha} |\alpha\rangle\langle\alpha|\vec{k}\rangle, \tag{4.6}$$

where

$\left|\vec{k}\right\rangle$ represents a normalized plane wave, $\frac{1}{\sqrt{\Omega}} e^{i\,\vec{k}\cdot\vec{r}}$, (Ω is considered volume)

$|\alpha\rangle$ represents a core wave function, $\varphi_{\alpha}(\vec{r})$.

It is easy to verify that $\left|\vec{k}\right\rangle_{OPW}$ is orthogonal to any core states, that is,

$$\begin{aligned}\langle\alpha'|\vec{k}\rangle_{OPW} &= \langle\alpha'|\vec{k}\rangle - \sum \langle\alpha'|\alpha\rangle\langle\alpha|\vec{k}\rangle \\ &= 0.\end{aligned} \tag{4.7}$$

Introduce the projection operator,

$$\mathbf{P} = \sum_{\alpha} |\alpha\rangle\langle\alpha|, \tag{4.8}$$

substitute into the definition of the OPW,

$$\left|\vec{k}\right\rangle_{OPW} = (1 - \mathbf{P})\left|\vec{k}\right\rangle$$

and any conduction-band states can be expanded in terms of linear combinations of OPW as

$$\varphi_{\vec{k}} = \sum_{\vec{q}} a_{\vec{q}}(\vec{k}) \left|\vec{q} + \vec{k}\right\rangle_{OPW} = \sum_{\vec{q}} a_{\vec{q}}(\vec{k})(1 - \mathbf{P})\left|\vec{q} + \vec{k}\right\rangle. \tag{4.9}$$

(The sum is written this way so that $a_{\vec{q}}$ will be greatest for $\vec{q} = 0$ when $\varphi_{\vec{k}}$ is similar to $|\vec{k}\rangle_{OPW}$.) This form can be substituted into the Schrödinger equation to obtain.

$$\begin{gathered}\sum_{\vec{q}} a_{\vec{q}}(\vec{k})\mathbf{H}|\vec{q}+\vec{k}\rangle_{OPW} = E_{\vec{k}} \sum_{\vec{q}} a_{\vec{q}}(\vec{k})|\vec{q}+\vec{k}\rangle_{OPW} \\ \sum_{\vec{q}} a_{\vec{q}}(\vec{k})(\mathbf{T}+V(\vec{r}))(\mathbf{1}-\mathbf{P})|\vec{q}+\vec{k}\rangle = E_{\vec{k}} \sum_{\vec{q}} a_{\vec{q}}(\vec{k})(\mathbf{1}-\mathbf{P})|\vec{q}+\vec{k}\rangle .\end{gathered} \tag{4.10}$$

Re-arrange all terms to the left side, except the term with $E_{\vec{k}}$ alone:

$$\mathbf{T}\sum_{\vec{q}} a_{\vec{q}}(\vec{k})|\vec{q}+\vec{k}\rangle + \left[V(\vec{r}) + E_{\vec{k}}\mathbf{P} - \mathbf{HP}\right]\sum_{\vec{q}} a_{\vec{q}}(\vec{k})|\vec{q}+\vec{k}\rangle = E_{\vec{k}}\sum_{\vec{q}} a_{\vec{q}}(\vec{k})|\vec{q}+\vec{k}\rangle . \tag{4.11}$$

Let

$$\begin{aligned}\mathbf{W} &= V(\vec{r}) + \left(E_{\vec{k}} - \mathbf{H}\right)\mathbf{P} \\ \phi_{\vec{k}} &= \sum_{\vec{q}} a_{\vec{q}}(\vec{k})|\vec{q}+\vec{k}\rangle\end{aligned} \tag{4.12}$$

we obtain

$$\mathbf{T}\phi_{\vec{k}} + \mathbf{W}\phi_{\vec{k}} = E_{\vec{k}}\phi_{\vec{k}} \tag{4.13}$$

where W is called the pseudopotential and $\phi_{\vec{k}}$ is called the pseudo wave function. The true wave function is related to the *pseudo wave function* by

$$\varphi_{\vec{k}} = (\mathbf{1}-\mathbf{P})\phi_{\vec{k}} .$$

4.3.2 Diffraction model

Analogous to

$$V(\vec{r}) = \sum_{j} v(|\vec{r} - \vec{r}_j|), \tag{4.14}$$

where $\vec{r}_j$ is the positioning vector of a core ion, we can write the pseudopotential as

$$\mathbf{W}(\vec{r}) = \sum_{j} \mathrm{w}(|\vec{r} - \vec{r}_j|), \tag{4.15}$$

and the one-electron pseudo wave function, Φ, must satisfy the equation

$$[\mathbf{T} + \mathbf{W}]\Phi = i\hbar \frac{\partial}{\partial t}\Phi \ . \tag{4.16}$$

The most convenient choice of boundary condition is a periodic boundary condition. The cubic box with edge length L is replicated throughout space to form an infinite lattice. However, the ions themselves are not required to form a periodic array. The time dependence can be factored out by writing the wave function in the form

$$\Phi(\vec{r}, t) = \phi(\vec{r}) \cdot e^{-iEt/\hbar} \tag{4.17}$$

Then we can obtain

$$[\mathbf{T} + \mathbf{W}]\Phi = E\Phi \, . \tag{4.18}$$

In a perturbation theory approximation, we consider the unperturbed Hamiltonian to be **T**, and **W** to be a small perturbation, so the perturbed Hamiltonian is **T**+ **W**. Then we write

$$\begin{aligned} \phi &= \phi^{(0)} + \phi^{(1)} + \phi^{(2)} + \ldots \\ E &= E^{(0)} + E^{(1)} + E^{(2)} + \ldots \ . \end{aligned} \tag{4.19}$$

They can be substituted into the pseudo wave equation to get the result separated by order:

$$\begin{aligned} \mathbf{T}\phi^{(0)} &= E^{(0)}\phi^{(0)} \\ \mathbf{T}\phi^{(1)} + \mathbf{W}\phi^{(0)} &= E^{(0)}\phi^{(1)} + E^{(1)}\phi^{(0)} \\ \mathbf{T}\phi^{(2)} + \mathbf{W}\phi^{(1)} &= E^{(0)}\phi^{(2)} + E^{(1)}\phi^{(1)} + E^{(2)}\phi^{(0)} \\ \vdots \qquad \vdots \quad &= \quad \vdots \qquad\qquad\qquad \vdots \ . \end{aligned} \tag{4.20}$$

For the system of volume Ω, the zero-order equation can be solved easily to obtain plane wave solution,

$$\phi^{(0)} = \frac{1}{\sqrt{\Omega}} e^{i\,\vec{k}\cdot\vec{r}} = \left|\vec{k}\right\rangle, \tag{4.21}$$

with the eigenvalue

$$E^{(0)} = \frac{\hbar^2 k^2}{2m}. \tag{4.22}$$

Since the zero-order solutions, $\phi^{(0)}$, form a complete set, we can expand the wave function in terms of

$$\phi_{\vec{k}} = \sum_{\vec{q}} a_{\vec{q}}(\vec{k}) \left|\vec{q} + \vec{k}\right\rangle , \tag{4.23}$$

where the first order coefficients for $\vec{q} \neq 0$ is

$$a_{\vec{q}}\left(\vec{k}\right) = \frac{\left\langle \vec{k} + \vec{q} \middle| \mathbf{W} \middle| \vec{k} \right\rangle}{\frac{\hbar^2}{2m}\left(k^2 - \left|\vec{k} + \vec{q}\right|^2\right)}.$$

Substituting into the first- and second-order equations we obtain

$$\begin{aligned} E^{(1)}(\vec{k}) &= \left\langle \vec{k} \middle| \mathbf{W}(\vec{r}) \middle| \vec{k} \right\rangle \\ E^{(2)}(\vec{k}) &= \sum_{\vec{q}\neq 0} \frac{\left\langle \vec{k} + \vec{q} \middle| \mathbf{W}(\vec{r}) \middle| \vec{k} \right\rangle \left\langle \vec{k} \middle| \mathbf{W}(\vec{r}) \middle| \vec{k} + \vec{q} \right\rangle}{\frac{\hbar^2}{2m}\left(k^2 - \left|\vec{k} + \vec{q}\right|^2\right)}. \end{aligned} \tag{4.24}$$

We can calculate $\left\langle \vec{k} + \vec{q} \middle| \mathbf{W}(\vec{r}) \middle| \vec{k} \right\rangle$:

$$\begin{aligned} \left\langle \vec{k} + \vec{q} \middle| \mathbf{W}(\vec{r}) \middle| \vec{k} \right\rangle &= \frac{1}{\Omega} \sum_j e^{i\vec{q}\cdot\vec{r}} \int e^{i(\vec{k}+\vec{q})\cdot(\vec{r}-\vec{r}_j)} \mathbf{w}(\vec{r} - \vec{r}_j) e^{i\,\vec{k}\cdot(\vec{r}-\vec{r}_j)}\, d\tau \\ &= \mathrm{S}(\vec{q}) \left\langle \vec{k} + \vec{q} \middle| \mathbf{w} \middle| \vec{k} \right\rangle, \end{aligned} \tag{4.25}$$

where $\mathrm{S}(\vec{q}) = \frac{1}{N} \sum_j e^{-i\,\vec{q}\cdot\vec{r}_j}$ is the structure factor, and

$\langle \vec{k}+\vec{q}|\mathbf{w}|\vec{k}\rangle = \frac{1}{\Omega_0}\int e^{-i(\vec{k}+\vec{q})\cdot\vec{r}}\,w(\vec{r})\,e^{-i\vec{k}\cdot\vec{r}}\,d\tau$ is the form factor. Here Ω_0 is the volume per ion, Ω/N. The total electron energy for $\phi_{\vec{k}}$ can be written

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m} + \langle \vec{k}|\mathbf{W}|\vec{k}\rangle + \sum_{\vec{q}\neq 0} \frac{\langle \vec{k}+\vec{q}|\mathbf{W}|\vec{k}\rangle\langle \vec{k}|\mathbf{W}|\vec{k}+\vec{q}\rangle}{\frac{\hbar^2}{2m}\left(k^2-|\vec{k}+\vec{q}|^2\right)}$$

$$= \frac{\hbar^2 k^2}{2m} + \mathrm{S}(\vec{q}=0)\langle \vec{k}|\mathbf{w}|\vec{k}\rangle + \sum_{\vec{q}\neq 0} \frac{\mathrm{S}^*(\vec{q})\mathrm{S}(\vec{q})\langle \vec{k}+\vec{q}|\mathbf{w}|\vec{k}\rangle\langle \vec{k}|\mathbf{w}|\vec{k}+\vec{q}\rangle}{\frac{\hbar^2}{2m}\left(k^2-|\vec{k}+\vec{q}|^2\right)} \qquad \text{... ... (4.26)}$$

and the total energy per ion can be calculated by summing over all electron states in the Fermi sphere:

$$E = \frac{1}{N}\sum_{k\langle k_F} E(\vec{k}) = \frac{2\Omega}{(2\pi)^3}\int_{k\langle k_F} E(\vec{k})\,d^3k$$

$$= \tfrac{3}{5}Z\frac{\hbar^2 k_F^2}{2m} + Z\overline{\langle \vec{k}|\mathbf{w}|\vec{k}\rangle} + \sum_{\vec{q}\neq 0}\mathrm{S}^*(\vec{q})\mathrm{S}(\vec{q})\frac{2\Omega}{(2\pi)^3}\int_{k<k_F}\frac{\langle \vec{k}+\vec{q}|\mathbf{w}|\vec{k}\rangle\langle \vec{k}|\mathbf{w}|\vec{k}+\vec{q}\rangle}{\frac{\hbar^2}{2m}\left(k^2-|\vec{k}+\vec{q}|^2\right)}d^3k \qquad \text{...... (4.27)}$$

The third term in the electron energy is called the band-structure energy, where the expression to the right of $\mathrm{S}^*(\vec{q})\mathrm{S}(\vec{q})$ is called energy-wavenumber characteristic function, $F(\vec{q})$:

$$F(\vec{q}) = \frac{2\Omega}{(2\pi)^3}\int_{k<k_F}\frac{\langle \vec{k}+\vec{q}|\mathbf{w}|\vec{k}\rangle\langle \vec{k}|\mathbf{w}|\vec{k}+\vec{q}\rangle}{\frac{\hbar^2}{2m}\left(k^2-|\vec{k}+\vec{q}|^2\right)}d^3k, \qquad (4.28)$$

and the band-structure energy may be written

$$E_{bs} = \sum_{\vec{q}\neq 0} S^*(\vec{q})S(\vec{q})F(\vec{q}). \qquad (4.29)$$

Explicitly written,

$$\begin{aligned} E_{bs} &= \sum_{\vec{q}\neq 0}\sum_{ij}\frac{1}{N^2}e^{-\vec{q}\cdot(\vec{r}_i-\vec{r}_j)}F(\vec{q}) \\ &= \sum_{\vec{q}\neq 0}\sum_{i\neq j}\frac{1}{N^2}e^{-\vec{q}\cdot(\vec{r}_i-\vec{r}_j)}F(\vec{q})+\sum_{\vec{q}\neq 0}\frac{1}{N}F(\vec{q}) \\ &= \frac{1}{2\mathrm{N}}\sum_{\mathrm{i}\neq\mathrm{j}}\mathrm{V}_{\mathrm{ind}}(\vec{r}_i-\vec{r}_j)+\sum_{\vec{q}\neq 0}\frac{1}{N}F(\vec{q}), \end{aligned} \tag{4.30}$$

where

$$V_{ind}(\vec{r})=\frac{2}{N}\sum_{\vec{q}\neq 0}F(\vec{q})e^{-i\,\vec{q}\cdot\vec{r}}\,. \tag{4.31}$$

It can be seen that only the value of the first term changes as a function of the arrangement of the ions. Thus we can say that $V_{ind}(\vec{r})$ represent the effective interaction between ions separated by $\vec{r}$. By converting the sum to an integral, using $\sum_k f=\Omega/(2\pi)^3\int f\,d^3k$, we obtain

$$V_{ind}(R)=\frac{\Omega_0}{\pi^2}\int_0^\infty F(q)\frac{\sin qR}{R}q\,dq \tag{4.32}$$

4.3.3 Self-consistent screening pseudopotential of electrons.

To include the effects of electron-electron interactions, the potential due to rapidly moving electrons is replaced, approximately, by a time average which is computed from the distribution of the probability at a given potential determined by the square of the wave function. This approximate potential is called the self-consistent field, denoted by $\mathbf{W}^1(\vec{r})$. The total potential seen by the electrons is

$$\mathbf{W}(\vec{r})=\mathbf{W}^0(\vec{r})+\mathbf{W}^1(\vec{r})\,, \tag{4.33}$$

where

$$\begin{aligned} \mathbf{W}^0(\vec{r}) &= \sum_j \mathrm{w}(\vec{r}-\vec{r}_j) \\ &= \text{potential due to ion cores.} \end{aligned} \tag{4.34}$$

The electron density can be computed from $\varphi^{*}\varphi$, where $\varphi_{\bar{k}}$ is the true wave function as derived from

$$\varphi_{\bar{k}} = \sum_{\bar{q}} a_{\bar{q}}(\bar{k})\left|\bar{q}+\bar{k}\right\rangle. \tag{4.35}$$

Thus,

$$\varphi^{*}\varphi = \tfrac{1}{\Omega}\left[1 + \sum_{\bar{q}\neq 0}\left(a_{\bar{q}}\left(\bar{k}\right)e^{i\bar{q}\cdot\bar{r}} + a_{\bar{q}}^{*}\left(\bar{k}\right)e^{-i\bar{q}\cdot\bar{r}}\right)+\ldots\right]. \tag{4.36}$$

Summing over for all electron states in the Fermi sphere to obtain the total electron density (the constant term is omitted because it is the same for all electrons and provides a uniform negative charge distribution)

$$n(\bar{r}) = \frac{2}{(2\pi)^{3}}\sum_{\bar{q}\neq 0}\int_{k<k_F}\left(a_{\bar{q}}\left(\bar{k}\right)e^{i\bar{q}\cdot\bar{r}} + a_{\bar{q}}^{*}\left(\bar{k}\right)e^{-i\bar{q}\cdot\bar{r}}\right)d^{3}k \tag{4.37}$$

we examine $n(\bar{r})$ written in terms of a Fourier expansion:

$$n(\bar{r}) = \sum_{\bar{q}\neq 0} n_{\bar{q}}e^{i\bar{q}\cdot\bar{r}}. \tag{4.38}$$

It can be seen that

$$n_{\bar{q}} = \frac{2}{(2\pi)^{3}}\int_{k<k_F}\left(a_{\bar{q}}\left(\bar{k}\right) + a_{-\bar{q}}^{*}\left(\bar{k}\right)\right)d^{3}k. \tag{4.39}$$

where

$$a_{\bar{q}}\left(\bar{k}\right) = \frac{\left\langle\bar{k}+\bar{q}\right|\mathbf{W}\left|\bar{k}\right\rangle}{\frac{\hbar^{2}}{2m}\left(k^{2}-\left|\bar{k}+\bar{q}\right|^{2}\right)} \tag{4.40}$$

$$n_{\vec{q}} = \frac{4}{(2\pi)^3} \int \frac{\langle \vec{k}+\vec{q}|\mathbf{W}|\vec{k}\rangle}{\frac{\hbar^2}{2m}\left(k^2 - \left|\vec{k}+\vec{q}\right|^2\right)} d^3k . \tag{4.41}$$

For the so-called Hartree dielectric function, we assume that W is a local potential, and $\langle \vec{k}+\vec{q}|\mathbf{W}|\vec{k}\rangle$ is independent of $\vec{k}$. Then it can be taken out from the integral, and from an integration table

$$\int\limits_{k<k_F} \frac{1}{k^2 - \left|\vec{k}+\vec{q}\right|^2} dk^3 = -\frac{\pi k_F}{2}\left(1 + \frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\right), \tag{4.42}$$

where

$$\eta = \frac{q}{2k_F}.$$

Then we can obtain the electron distribution function in Fourier space:

$$n_{\vec{q}} = \frac{-mk_F\langle \vec{k}+\vec{q}|\mathbf{W}|\vec{k}\rangle}{2\pi^2\hbar^2}\left(1 + \frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\right), \tag{4.43}$$

Comparing with the Poisson equation in Fourier space

$$q^2\mathbf{W}^1_{\vec{q}} = 4\pi e^2 n_{\vec{q}}, \tag{4.44}$$

where total potential seen by the electron is $\mathbf{W} = \mathbf{W}^0 + \mathbf{W}^1$. We can define the dielectric function ε(q) by

$$\langle \vec{k}+\vec{q}|\mathbf{W}|\vec{k}\rangle = \langle \vec{k}+\vec{q}|\mathbf{W}^0|\vec{k}\rangle\frac{1}{\varepsilon(q)}, \tag{4.45}$$

so

$$\varepsilon(q) = 1 + \frac{me^2}{2\pi k_F\hbar^2\eta^2}\left(1 + \frac{1-\eta}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\right). \tag{4.46}$$

This form can also be applied to the form factors

$$\langle \vec{k}+\vec{q}|\mathrm{w}|\vec{k}\rangle = \frac{\langle \vec{k}+\vec{q}|\mathrm{w}^{0}|\vec{k}\rangle}{\varepsilon(q)} . \tag{4.47}$$

The total energy due to electron-electron interactions is given by

$$\begin{aligned} E_{elec-elec} &= \int n(\vec{r})\mathrm{W}'(\vec{r})\,d\tau \\ &= \frac{q^{2}\Omega}{8\pi e^{2}}\sum_{\vec{q}\neq 0}\mathrm{W}_{q}^{1^{*}}\mathrm{W}_{q}^{1} . \end{aligned} \tag{4.48}$$

Incorporating this with the band-structure energy, we obtain

$$\begin{aligned} F(\vec{q}) &= \frac{2\Omega}{(2\pi)^{3}}\int \frac{\langle \vec{k}|\mathrm{w}|\vec{k}+\vec{q}\rangle\langle \vec{k}+\vec{q}|\mathrm{w}|\vec{k}\rangle}{\frac{\hbar^{2}}{2m}\left(k^{2}-|\vec{k}+\vec{q}|^{2}\right)}\,dk^{3} - \frac{q^{2}\Omega}{8\pi e^{2}}\mathrm{w}_{q}^{1^{*}}\mathrm{w}_{q}^{1} \\ &= -\frac{q^{2}\Omega}{8\pi e^{2}}\left|\langle \vec{k}+\vec{q}|\mathrm{w}|\vec{k}\rangle\right|^{2}\left(\varepsilon(q)-1\right) - \frac{q^{2}\Omega}{8\pi e^{2}}\left|\langle \vec{k}+\vec{q}|\mathrm{w}^{1}|\vec{k}\rangle\right|^{2} \\ &= -\frac{q^{2}\Omega}{8\pi e^{2}}\left|\langle \vec{k}+\vec{q}|\mathrm{w}^{0}|\vec{k}\rangle\right|^{2}\frac{\varepsilon(q)-1}{\varepsilon(q)} . \end{aligned}$$

...... (4.49)

4.3.4 Form factor

4.3.4.1 Point ion model

In this model, the ion is reduced to a point. There are two contributions to the potential: the Coulomb potential and delta-function repulsion at the nucleus. The latter contribution can be derived from the exclusion of conduction electrons from the core region and written as

$$\mathrm{w}^{0}(\vec{r}) = -\frac{Ze^{2}}{r} + \beta\delta(\vec{r}) \tag{4.50}$$

where β is the strength of the repulsion. Thus we obtain

$$\begin{aligned}\langle \vec{k}+\vec{q}|\mathrm{w}^0(\vec{r})|\vec{k}\rangle &= \frac{1}{\Omega}\int\left(-\frac{Ze^2}{r}+\beta\,\delta(\vec{r})\right)e^{-i\vec{q}\cdot\vec{r}} \\ &= -\frac{4\pi Ze^2}{q^2\Omega}+\frac{\beta}{\Omega}.\end{aligned} \tag{4.51}$$

4.3.4.2 Ashcroft model

The Ashcroft model [Gurskii et al. 1993] was proposed to represent the interaction in the form

$$w_H(q) = -\frac{4\pi z_H}{\Omega q^2} \tag{4.52}$$

$$w_j(q) = -\frac{4\pi z_j}{\Omega q^2}\cos(q\,r_{c,j}) \tag{4.53}$$

where H represents the hydrogen atom and j represents other atoms or ions with an effective radius of ion core r_c.

4.3.5 Dielectric functions

The three models of dielectric functions used in this study (each of which is derived from different assumptions) are:

4.3.5.1 Hartree dielectric function

$$\varepsilon(q) = 1+\frac{me^2}{2\pi k_F \hbar^2\eta^2}\left(1+\frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\right) \tag{4.54}$$

[Harrison 1963].

4.3.5.2 Gurskii dielectric function

$$\varepsilon(q) = 1+\frac{4\pi}{q^2}\Pi(q) \tag{4.55}$$

$$\Pi(q) = \frac{\Pi_0(q)}{1 - \left(4\pi/q^2\right)G(x)\Pi_0(q)} \tag{4.56}$$

$$\Pi_0(q) = \frac{2}{(2\pi)^3}\int \frac{n\left(E_{\vec{k}}\right) - n\left(E_{\vec{k}+\vec{q}}\right)}{\frac{1}{2}\left|\vec{k}+\vec{q}\right|^2 - \frac{1}{2}k^2} d^3k \tag{4.57}$$

$$G(x) = \frac{1}{2}\frac{x^2}{x^2 + 2\left(1 + 0.153\eta^2\right)^{-1}} \tag{4.58}$$

where

$n\left(E_{\vec{k}}\right) = \left[\exp\left(\dfrac{\frac{1}{2}k^2 - \mu}{k_B T}\right) + 1\right]^{-1}$ is Fermi distribution function,

μ is chemical potential can be obtained from solving

$$\frac{N_m}{\Omega} = \frac{1}{\pi^2}\int_0^\infty \frac{k^2 dk}{\exp\left[\left(\frac{1}{2}k^2 - \mu\right)/k_B T\right] + 1},$$

$x = \dfrac{q}{k_F}$, $\eta^2 = \dfrac{1}{\pi k_F}$, and $k_F = \left(\dfrac{3\pi^2 Z_m N_m}{\Omega}\right)^{1/3}$.

[Gurskii et al. 1993].

4.3.5.3 Ichimaru dielectric function

$$\varepsilon(q) = 1 + \frac{4\pi}{q^2}\Pi(q) \tag{4.59}$$

$$\Pi(q) = \frac{k}{\pi^2}\frac{f(x)}{1 - \left(4\mu^2/x^2\right)G(x)f(x)} \tag{4.60}$$

$$f(x) = \frac{1}{2} + \frac{4 - x^2}{8x}\ln\left|\frac{2+x}{2-x}\right| \tag{4.61}$$

$$G(x) = Ax^4 + Bx^2 + C + \left(Ax^4 + \left(B + \tfrac{8}{3}A\right)x^2 - C\right)\left(\frac{4k_F - q^2}{4k_F q}\ln\left|\frac{2k_F + q}{2k_F - q}\right|\right) \tag{4.62}$$

$$A = 0.029$$

$$B = \tfrac{9}{16}\gamma_0\left(r_S\right) - \tfrac{3}{64}\left[1 - g(0)\right] - \tfrac{16}{15}A$$

$$C = -\tfrac{3}{4}\gamma_0\left(r_S\right) - \tfrac{9}{16}\left[1 - g(0)\right] - \tfrac{16}{15}A$$

$g(0) = \frac{1}{8}\left(\dfrac{Z}{\mathrm{I}_1(Z)}\right)^2$ I_1 = modified Bessel funtion.

$$Z = 4\left(\frac{\lambda r_S}{\pi}\right)^{1/2}, \qquad \lambda = \left(\frac{4}{9\pi}\right)^{1/3}, \qquad r_S = \frac{1}{\lambda k_F}$$

$$\gamma_0(r_S) = \frac{1}{4} + \frac{\frac{\lambda\pi}{8} d_0 y_2 \left[1 + 2d_1 y_1 + \left(\frac{4}{3}d_2 + d_1^2\right)y_2 + \left(\frac{3}{2}d_3 + \frac{7}{6}d_1 d_2\right)y_3 + \frac{4}{3}d_1 d_3 y_2^2\right]}{\left[1 + d_1 y_1 + d_2 y_2 + d_3 y_3\right]^2}$$

$$d_0 = 0.06218 \quad d_2 = 2.82224$$

$$d_1 = 9.81379 \quad d_3 = 0.73641$$

$$y_1 = r_S^{1/2}, \qquad y_2 = r_S, \qquad y_3 = r_S^{3/2}$$

where

$$x = \frac{q}{k_F}, \qquad \mu^2 = \frac{1}{\pi k_F}, \qquad k_F = \left(\frac{3\pi^2 Z_m N_m}{\Omega}\right)^{1/3}$$

[Ichimaru and Utsumi 1981].