Electronic structure of an ion in liquid metallic lithium treated as a nucleus–electron mixture

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Abstract. A set of integral equations for determining the liquid and electronic ion structures in a liquid metal have been derived by treating a liquid metal as a nucleus–electron mixture. By these integral equations with the atomic number as the only input, an electronic excited state of an ion in a liquid metal can be determined in a self-consistent way with the ion and valence–electron density distributions around it. It is shown that our integral equations lead to a liquid-state version of the spherical-solid model proposed by Almbladh and von Barth to treat the spectroscopic problem in a solid. The integral equations combined with Slater's transition state method are applied to evaluate the K-edge position of a liquid metallic lithium: the value 51.36 eV is obtained at 470 K, which is compared with the experimental one of 51.26 eV. Thus it is ascertained that our integral equations can determine precisely the electronic structure of an ion as well as the liquid structure without the use of any information other than the atomic number.

1. Introduction

Calculating the electronic states of an atom immersed in a liquid metal is a complex problem when compared to the calculation of the electronic structure of an atom in vacuum, since the atomic structure must be determined to be consistent with the liquid structure which is specified by the valence-electron density and ion density distributions around the atom under investigation. Similarly, a constituent ion of a liquid metal behaves as a dissolved impurity in a liquid metal when its core electrons are in an excited state, or especially when it contains core holes so as to have a different ionic charge from constituent ions (we will refer to this ion as the tagged ion). Therefore, in treating the spectroscopic problem concerning an ion in a liquid metal, the internal electronic structure of the excited ion (tagged ion) is to be determined in a consistent way with the screening due to the surrounding electrons and ions, of which the effects are represented by the radial distribution function (RDF) between valence-electron and tagged ion, $g_{eT}(r)$, and the RDF between constituent ion and tagged ion, $g_{IT}(r)$. That is, the spectroscopic calculation of a liquid metal has to combine two problems: the 'external' one to determine the liquid structure, and the 'internal' one to calculate the atomic structure under this circumstance. As a consequence of this difficulty, to date there is no standard approach to the spectroscopic calculation for a liquid metal.

Previously, by applying the density functional theory to a liquid metal modelled as a nucleus–electron mixture, we have derived a set of integral equations which provide

both the liquid structure as an electron–ion mixture, and the internal electronic structure of a constituent ion at the same time in a self-consistent manner (Chihara 1985). Recently, we have applied this formulation to a liquid metallic lithium and obtained the RDFs at two temperatures with the use of the atomic number Z_A as the only input data: the structure factors derived from our RDFs show excellent agreement with experimental results (Chihara 1989). At this stage, it is of interest to examine how exactly our formulation can describe the internal electronic structure (atomic structure) of an ion in a liquid metal in addition to the liquid structure. For this purpose we apply in the present paper our formulation to the calculation of the threshold energy of the K-edge observed in the soft x-ray emission and absorption spectra in a liquid metallic lithium: the K-emission and absorption spectra are observed when an electron in the valence state drops down to fill a hole in the K-shell (1s level) and an electron is transferred from the K-shell to a conduction state, respectively.

Almbladh and von Barth (1976) proposed the spherical-solid model (SSM) to calculate electronic states of an atom immersed in a solid. In this model, the potential felt by an electron caused by the ions around the atom under investigation is constructed by the spherical average of the ion potentials where the electron–ion interaction is assumed to be a pseudopotential. The model has been applied successfully to a variety of impurity problems by Manninen and Nieminen (1979, 1981), Perrot (1977a, 1977b) and Perrot and Rasolt (1982). Moreover, Fairlie and Greenwood (1983) modified the SSM to be applicable to a liquid metal by expressing the surrounding ion configuration in terms of the RDF around the impurity. In this respect, our method is shown to be identical to that of Fairlie and Greenwood except that in our method the pseudopotential and the interaction between ion and tagged particle (impurity) can be obtained self-consistently from the atomic number as the only input data, as will be mentioned later. Furthermore, the spherical-solid model reduces to the jellium–vacancy model when we introduce two further approximations: first the effect of the surrounding ions is replaced by the jellium with a spherical vacancy having the Wigner–Seitz radius R_{WS} at the centre, and secondly a pseudopotential is approximated as the pure coulombic potential $-Z_I e^2/r$ with the ionic charge Z_I. This simple model has been applied to the calculation of electronic states of an impurity in a solid by various investigators (for example, Nieminen and Puska (1980, 1982) and Rantala (1983)). This model can give a fairly good description of the electronic structure of an impurity in a solid where the surrounding ions do not relax significantly when the internal electronic state of the central impurity changes. However, this model may not be appropriate to treat an impurity in a liquid for some situation where the central impurity with core holes, for example, rearranges the surrounding ion distribution from $g_{Iimp}(r)$ to $g_{IT}(r)$ when its ionic charge Z_{imp} becomes Z_T (where $Z_{imp} \neq Z_T$). In the next section, the formulation to treat the spectroscopy of a liquid metal is presented in conjunction with integral equations for determining the usual liquid structure, which provide necessary data for the spectroscopic calculation. Calculated results for the K-edge in liquid Li are presented in section 3. The final section is devoted to a discussion.

2. Formulation

Previously, it has been shown on the basis of the nucleus–electron mixture model that the ion–ion and electron–ion RDFs are given by the following set of equations (Chihara 1985)

$$g_{II}(r) = \exp(-\beta v_{II}^{eff}(r)) \tag{1}$$

$$g_{eI}(r) = n_e^{0v}(r|v_{eI}^{eff})/n_0^e. \tag{2}$$

In the above, $n_e^{0v}(r|U)$ is the valence-electron part of the total electron density distribution of the non-interacting electron gas with density n_0^e under external potential $U(r)$, which is calculated by solving the wave equation

$$[-(\hbar^2/2m)\nabla^2 + U(r)]\varphi_l(r) = \varepsilon_l\varphi_l(r) \tag{3}$$

in the form

$$n_e^0(r|U) \equiv \sum_l f(\varepsilon_l)|\varphi_l(r)|^2 = n_e^{0b}(r|U) + n_e^{0v}(r|U) \tag{4}$$

with

$$f(\varepsilon) \equiv \{\exp[\beta(\varepsilon - \mu_e^0)] + 1\}^{-1} \tag{5}$$

in conjunction with the bound electron density $n_e^{0b}(r|U)$. Effective interactions in (1) and (2) are represented as

$$v_{ij}^{eff}(r) = v_{ij}(r) - \Gamma_{ij}(r)/\beta - B_{ij}(r)/\beta \tag{6}$$

with

$$\Gamma_{ij}(r) \equiv \sum_l n_0^l \int C_{il}(|r - r'|)(g_{lj}(r') - 1)\,dr' \tag{7}$$

in terms of the bridge functions $B_{ij}(r)$ and the direct correlation functions (DCF) $C_{ij}(r)$. The bare electron–electron and the bare electron–ion interactions in (6) are given by the pure coulombic $v_{ee}(r) \equiv e^2/r$ and

$$v_{eI}(r) \equiv -Z_A e^2/r + \int v_{ee}(|r - r'|)n_e^b(r'|N)\,dr'$$

$$+ \mu_{xc}(n_e^b(r|N) + n_0^e) - \mu_{xc}(n_0^e) \tag{8}$$

respectively, with the use of the bound-electron density $n_e^b(r|N)$ and the exchange–correlation potential μ_{xc}. Here, the DCF $C_{ee}(r)$ is approximated by that of the jellium model in terms of the local-field correction factor $G_{ee}(Q)$, and the ion–ion bridge function $B_{II}(r)$ by that of the Percus–Yevick equation for the hard-spheres by neglecting $B_{eI}(r)$. Under these approximations, the above equations constitute a set of self-consistent equations for $g_{II}(r)$ and $g_{eI}(r)$ ($C_{II}(r)$ and $C_{eI}(r)$) on behalf of the Ornstein–Zernike (OZ) relations for the ion–electron mixture

$$g_{II}(r) - 1 = C_{II}(r) + \Gamma_{II}(r) \tag{9}$$

$$g_{eI}(r) - 1 = \hat{B}C_{eI}(r) + \hat{B}\Gamma_{eI}(r) \tag{10}$$

where $\hat{B}$ denotes an operator defined by

$$\mathscr{F}_Q(\hat{B}^\alpha f(r)) \equiv (\chi_Q^0)^\alpha \mathscr{F}_Q(f(r)) = (\chi_Q^0)^\alpha \int e^{iQ\cdot r}f(r)\,dr \tag{11}$$

for an arbitrary real number α.

We have applied this set of integral equations to a liquid metallic lithium and have obtained the ion–ion structure factors and the RDFs, which show good agreement with the experimental results (Chihara 1989). These integral equations can give the bound-electron density distribution around the ion in a liquid metal as well as the ion–ion and electron–ion RDFs, but there is no physical meaning for the bound energy levels obtained from (3) with $U(r) = v_{eI}^{eff}(r)$, since these equations are derived from the density functional

theory. Therefore, some method is necessary to extract the spectroscopic information from these integral equations. A bound level (1s) of a Li ion in a liquid metal can be observed as the K-edge in the soft x-ray experiments. The removal energy, I, of one 1s electron from the ion in a liquid metallic lithium is defined by the difference of the total energies between the initial state with an occupation number $n_{1s} = 2$ and a final $n_{1s} = 1$ state. Slater (1974) suggested that this energy difference can be calculated approximately from the one-electron energy level ε_{1s} in a transition state, which is defined as a state where the occupation number is halfway between those of the initial and final states, as is described by the relation

$$I = E[n_{1s} = 2] - E[n_{1s} = 1] = \int_1^2 \varepsilon_{1s}(n)\, \mathrm{d}n \simeq \varepsilon_{1s}(n_{1s} = 1.5). \tag{12}$$

In order to treat an ion in the transition state (the tagged lithium ion), we need a set of integral equations determining $g_{eT}(r)$, the RDF between the electron and the tagged ion with ionic charge $Z_T = 1.5$, and $g_{IT}(r)$—the RDF between constituent ion and tagged ion. The integral equations to treat a tagged ion with charge Z_T in a liquid metal have been obtained in the following forms (Chihara 1987):

$$g_{eT}(r) = n_e^{0v}(r|v_{eT}^{eff})/n_0^e \tag{13}$$

$$g_{IT}(r) = \exp(-\beta v_{IT}^{eff}(r)) \tag{14}$$

with effective interactions

$$v_{eT}^{eff}(r) = v_{eT}(r) + n_0^e \int \frac{C_{ee}(|r-r'|)}{-\beta}(g_{eT}(r') - 1)\, \mathrm{d}r'$$

$$+ n_0^I \int \frac{C_{eI}(|r-r'|)}{-\beta}(g_{IT}(r') - 1)\, \mathrm{d}r' \tag{15}$$

$$\equiv v_{eT}(r) - \Gamma_{eT}(r)/\beta \tag{16}$$

$$v_{IT}^{eff}(r) = Z_T Z_I e^2/r + n_0^e \int \frac{C_{Ie}(|r-r'|)}{-\beta}(g_{eT}(r') - 1)\, \mathrm{d}r'$$

$$+ n_0^I \int \frac{C_{II}(|r-r'|)}{-\beta}(g_{IT}(r') - 1)\, \mathrm{d}r' - B_{IT}(r)/\beta \tag{17}$$

$$\equiv Z_T Z_I e^2/r - \Gamma_{IT}(r)/\beta - B_{IT}(r)/\beta \tag{18}$$

where

$$v_{eT}(r) \equiv -Z_A e^2/r + \int v_{ee}(|r-r'|)n_e^b(r'|T)\, \mathrm{d}r'$$

$$+ \mu_{xc}(n_e^b(r|T) + n_0^e) - \mu_{xc}(n_0^e) \tag{19}$$

$$Z_T \equiv Z_A - \int n_e^b(r|T)\, \mathrm{d}r. \tag{20}$$

These integral equations are rewritten using the OZ relation in the forms for the DCFs.

$$\hat{B}C_{eT}(r) = n_e^{0v}(r|v_{eT} - \Gamma_{eT}/\beta)/n_0^e - 1 - \hat{B}\Gamma_{eT}(r) \tag{21}$$

$$C_{IT}(r) = \exp(-\beta v_{IT}(r) + \Gamma_{IT}(r) + B_{IT}(r)) - 1 - \Gamma_{IT}(r). \tag{22}$$

In the above expressions, the DCFs $C_{eI}(r)$ and $C_{II}(r)$ involved in $\Gamma_{eT}(r)$ and $\Gamma_{IT}(r)$ were already obtained when the RDFs $g_{eI}(r)$ and $g_{II}(r)$ were determined by solving (1) and (2). It is difficult to solve (21) and (22) directly for the case of a liquid metallic lithium where the plasma parameter Γ and the electron density paramenters, r_s, are so large that the coupling among ions and electrons is very strong. To circumvent this difficulty, we rewrite (22) into the form of the equations for a tagged particle immersed in a quasi-one-component liquid where the existence of electrons is eliminated by constructing an effective interaction between ion and tagged particle $\bar{v}_{IT}^{eff}(r)$ as follows:

$$\bar{C}_{IT}(r) = \exp(-\beta\bar{v}_{IT}^{eff}(r) + \gamma_{IT}(r) + B_{IT}(r)) - 1 - \gamma_{IT}(r) \tag{23}$$

where

$$\beta\bar{v}_{IT}^{eff}(Q) \equiv \beta 4\pi Z_I Z_T e^2/Q^2 - C_{Ie}(Q)C_{eT}(Q)n_0^e\chi_Q^0/(1 - n_0^e C_{ee}(Q)\chi_Q^0) \tag{24}$$

$$\gamma_{IT}(Q) \equiv n_0^I \bar{C}_{IT}(Q)\bar{C}_{II}(Q)/(1 - n_0^I \bar{C}_{II}(Q)) \tag{25}$$

with new functions

$$\bar{C}_{II}(Q) \equiv C_{II}(Q) + n_0^e |C_{eI}(Q)|^2 \chi_Q^e/(1 - n_0^e C_{ee}(Q)\chi_Q^0) \tag{26}$$

$$\bar{C}_{IT}(Q) \equiv C_{IT}(Q) + n_0^e C_{Ie}(Q)C_{eT}(Q)\chi_Q^0/(1 - n_0^e C_{ee}(Q)\chi_Q^0). \tag{27}$$

In this circumstance, the bound-electron levels in the tagged ion are obtained by solving a wave equation under the external potential

$$v_{eT}^{eff}(r) \equiv -Z_A e^2/r + \int v_{ee}(|r - r'|)n_e^b(r'|T)\,dr'$$

$$+ \mu_{xc}(n_e^b(r|T) + n_0^e) - \mu_{xc}(n_0^e) - \Gamma_{eT}(r)/\beta \tag{28}$$

which involves the influence of ions and electrons around it through $\Gamma_{eT}(r)$ defined in (16).

At this point, it should be mentioned that the effective potential (28) is rewritten by using the approximation

$$\mu_{xc}(n_e^b(r|T) + n_0^e) - \mu_{xc}(n_0^e) + \int \frac{C_{ee}^{xc}(|r - r'|)}{-\beta}(n_e^v(r'|T) - n_0^e)\,dr'$$

$$\simeq \mu_{xc}(n_e^b(r|T) + n_e^v(r|T)) - \mu_{xc}(n_0^e) \tag{29}$$

with $C_{ee}^{xc}(r) \equiv C_{ee}(r) + v_{ee}(r)$, in the form

$$v_{eT}^{eff}(r) \simeq -Z_A e^2/r + \int v_{ee}(|r - r'|)(n_e(r'|T) - n_0^e)\,dr' + \mu_{xc}(n_e(r|T))$$

$$- \mu_{xc}(n_0^e) + n_0^I \int \frac{C_{eI}(|r - r'|)}{-\beta}(g_{IT}(r') - 1)\,dr'. \tag{30}$$

As a result, this effective potential can be regarded as that of the SSM proposed by Almbladh and von Barth (1976) in the modified version to a liquid metal, since the DCF $-C_{eI}(r)/\beta$ plays the role of a psuedopotential. In other words, this approach is equivalent to the treatment of Fairlie and Greenwood (1983) except that in our method all quantities such as $g_{IT}(r)$ and the pseudopotential $-C_{eI}(r)/\beta$ can be given in a self-consistent manner without the use of any other information than the atomic number. Furthermore we can obtain the jellium–vacancy model by making the following two approximations in (30):
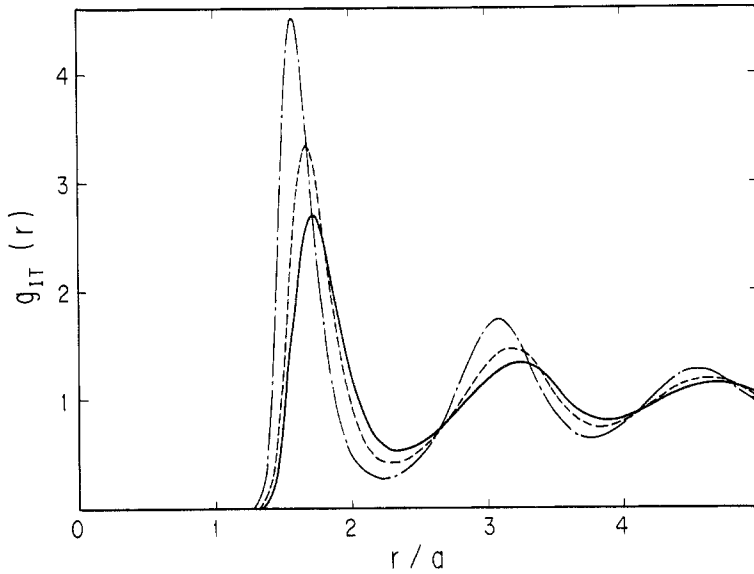
Figure 1. The ion density distributions around tagged ions with ionic charges $Z_T = 2, 1.5$ and 1, denoted by the chain, broken and full curves, respectively. The distance from the origin is represented in units of a, the mean distance between ions.

first, the neglect of the relaxation of ions surrounding the tagged particle during the emission and absorption processes, which is represented by $g_{IT}(r) \simeq g_{II}(r) \simeq \theta(r - R_{WS})$, in terms of the step function $\theta(r - R_{WS})$ with the Wigner–Seitz radius R_{WS}; and secondly, the random-phase approximation to the electron–ion DCF, $-C_{eI}(r)/\beta \simeq -Z_I e^2/r$.

It is important that the spin-polarisation effect is incorporated into the exchange-correlation potential for core electrons, since it brings about a significant difference in the evaluation of the excitation energy levels of the ion. Here, we use the local spin-density approximation (LSDA) to the potential only for the bound electrons

$$v_{eT}^{\mathrm{eff}\pm}(r) = -Z_A e^2/r + \int v_{ee}(|r - r'|) n_e^b(r'|T) \, dr'$$

$$+ \mu_{xc}^{\pm}(n_e^b(r|T), m_e^b(r|T)) - \mu_{xc}^{\pm}(n_0^c) - \Gamma_{eT}(r)/\beta \tag{31}$$

with $m_e^b(r|T) = n_e^{b+}(r|T) - n_e^{b-}(r|T)$ in terms of the up-spin and down-spin densities. However, the spin-polarisation effect is not considered in treating the valence electrons, that is, the potential for the valence electrons is taken to be of the LDA form as in (8).

3. Calculation of the K-edge in a liquid metallic lithium

The 1s bound-level of Li in a liquid metal can be observed as the K-edge position in the soft x-ray spectra. The position of the K-edge can be determined by the calculation of the 1s level of a tagged ion in the transition state $Z_T = 1.5$ in a liquid metallic Li as mentioned in the previous section. In this calculation, we use the same approximations made in the determination of the RDFs in a liquid metallic lithium (Chihara 1989). The bridge function $B_{II}(r)$ is approximated by that of the Percus–Yevick equation for the hard spheres of diameter σ with the packing fraction $\eta = \pi n \sigma^3/6$ and $B_{IT}(r) \simeq B_{II}(r)$.
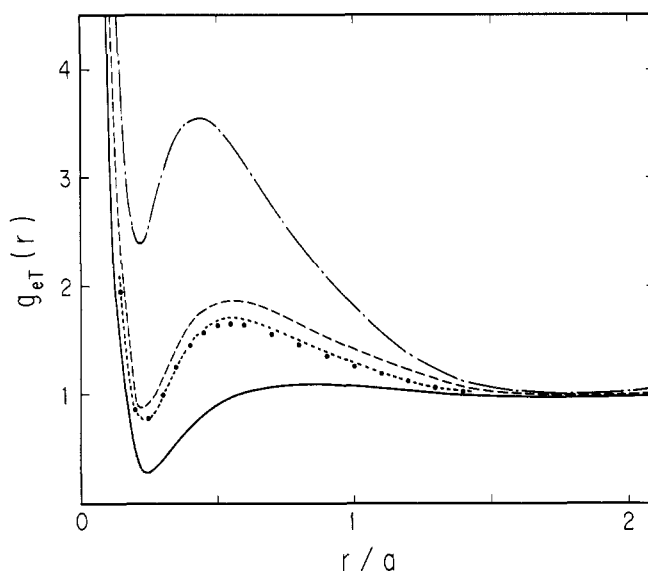
Figure 2. The valence-electron distributions around tagged ions with ionic charges $Z_T = 2$, 1.5 and 1: the chain, broken and full curves show the electron density distributions around ions with $Z_T = 2$, 1.5 and 1 under the ion distributions corresponding to figure 1, respectively. The short dashed curve displays the electron density distribution $g_{eT}(r)$ around an ion in the transition state $n_{1s} = 1.5$ under the fixed ion distribution as $g_{IT}(r) = g_{II}(r)$, while the full circles denote $g_{eT}(r)$ for the transition state calculated by the jellium–vacancy model.

The electron–electron DCF $C_{ee}(r)$ is approximated by that of the jellium model with the use of the local-field correction proposed by Geldart and Vosko (1966). The LDA and LSDA to the exchange–correlation potential are taken to be of the form proposed by Gunnarsson and Lundqvist (1976). Under these approximations, a set of integral equations (21)–(28) are solved for the tagged ions with $Z_T = 1.5$ (the transition state for the K-edge emission and absorption processes) and $Z_T = 2$, which corresponds to the tagged ion with one core-hole in the K-shell. The ion density distribution, $g_{IT}(r)$, and the electron density distribution, $g_{eT}(r)$, around the tagged ion with $Z = 1.5$ at a temperature of 470 K are shown in figures 1 and 2 by the broken curves, respectively, while those for $Z_T = 2$ are represented by the chain curves; for comparison, the ion–ion and electron–ion RDFs, $g_{II}(r)$ and $g_{eI}(r)$, of liquid Li are exhibited by the full curves in figures 1 and 2, respectively.

When a core electron of an ion in a liquid metal is transferred to a conduction state and the core-hole lifetime is sufficiently longer than the relaxation time for the surrounding ions to reach an equilibrium density distribution around it, the K-emission edge caused by a conduction electron falling into this hole must be determined under the constraint that the RDF $g_{II}(r)$ has been changed to $g_{IT}(r)$ with $Z_T = 2$ during the process to create a core-hole. However, if the core-hole lifetime is shorter than the relaxation time of the ions, we can use $g_{II}(r)$ to describe the ion distribution around the tagged ion which radiates the K-emission spectra. In this case, it is sufficient to take account of only the relaxation of the electron density distribution in the determination of the threshold energy of the K-emission; the short dashed curve in figure 2 shows the electron density distribution $g_{eT}(r)$ in the transition state with occupation number $n_{1s+} = 0.5$ and the fixed ion distribution $g_{II}(r)$ representing the ion distribution around the tagged ion. In this transition state, we obtain $\varepsilon_{1s+} = -51.33$ eV of which the absolute

value becomes the threshold energy for the K-emission, while the threshold energy is obtained as 51.36 eV in the transition state where the ion relaxation is considered by using $g_{IT}(r)$ with $Z_T = 1.5$. These two calculations do not yield a significant difference. If we adopt the jellium–vacancy model where the ion distribution around the tagged ion is fixed as $g_{IT}(r) = \theta(r - R_{WS})$ irrespective of Z_T, we get the electron density distribution $g_{eT}(r)$ around the tagged ion in the transition state $n_{1s+} = 0.5$, as shown by the full circles in figure 2. The threshold energy in this environment is 51.51 eV; this value shows a good estimation for the K-edge position in spite of the simplicity of the calculation.

On the other hand, Callcott in collaboration with Arakawa and Ederer (1977) and with Arakawa (1977) have observed the edge position of the K x-ray emission to be 54.91 eV at 493 K (the melting point of Li is 453.7 K). In the comparison of our computed results with the experimental values, it should be noted that the threshold energy determined from the soft x-ray emission and absorption experiments is measured from the Fermi energy level ε_F, while our calculated value is from the zero of the potential for electrons (the bottom of the band). As a result, the experimental value differs from the calculated one by the bandwidth, which is roughly estimated from the Fermi energy E_F of a free electron gas with the density parameter r_s of the conduction electrons in the system. In this connection, the band calculations by Lawrence (1971) and by Dagens and Perrot (1973) give the bandwidth $\varepsilon_F = 3.65$ and 3.54 eV, respectively, which show a great difference from the free electron value $E_F = 4.54$ eV at $r_s = 3.308$. On the other hand, from the soft x-ray spectra, Skinner (1940) obtained a bandwidth of 3.7 ± 0.5 eV. In addition, McMullen (1970) has analysed the K emission spectra of Li observed by Arita and Sagawa (1969) to obtain a bandwidth of $\varepsilon_F = 3.65$ eV. Therefore, here we take the value of the bandwidth to be 3.65 eV; then the threshold energy from the bottom of the band can be evaluated as $54.91 - 3.65 = 51.26$ eV. Consequently, our calculated values of 51.36 eV and 51.33 eV (obtained when $g_{II}(r)$ is not changed) are shown to be in excellent agreement with this experimental result, whether the relaxation effect of the surrounding ions is taken account of, or not.

It should be noted that the central tagged ion is neutralised in the whole space by pushing away the surrounding ions and by accumulating the conduction electrons so as to fulfil the neutrality relation

$$Z_T = -n_I^0 \int (g_{IT}(r) - 1)\, dr + n_e^0 \int (g_{eT}(r) - 1)\, dr. \tag{32}$$

The usual ion with $Z_I = 1$ in liquid Li at 470 K satisfies the relation: $1 = -(-0.97) + 0.03$, which shows that the central ion is screened mainly by the removed ions $g_{II}(r)$ rather than by collecting conduction electrons. On the other hand, the tagged ion with one core-hole is neutralised in such a way as to satisfy the relation: $2 = -1.19 + 3.19$, which means that the surrounding ions are attracted to the tagged ion so as to enhance the polarisation, and in consequence many conduction electrons are necessary to be piled-up so as to compensate for it as shown in figures 1 and 2 by the chain curves. The neutrality condition $1.5 = -(-0.03) + 1.47$ is obtained in the transition state with the use of $g_{IT}(r)$ with $Z_T = 1.5$ to represent the ion distribution around the tagged ion; the central ion is screened almost by accumulated conduction electrons. When the ion distribution around the tagged ion is fixed as $g_{II}(r)$, the neutrality relation is satisfied as $1.5 = -(-0.97) + 0.53$, which is quite similar to the case of the jellium–vacancy: $1.5 = -(-1) + 0.5$.

In table 1, the temperature dependence of the edge position is shown at three temperatures, along with the results based on the jellium–vacancy model. Also, we have

Table 1. The temperature dependence of the K-edge position of Li calculated by the LSDA full calculation and the jellium–vacancy model, which are compared with the LDA results. The thermal expansion is represented by the variation of r_s.

Temperature (K)	470	595	725
r_s	3.308	3.346	3.372
LSDA	51.36	51.53	51.67
LSDA (Jellium)	51.51	51.69	51.84
LDA	54.06	54.24	54.38

calculated the threshold energies of the K-edge at these three temperatures with the use of the LDA and have included these in the same table; the edge position calculated by the use of the LDA does not show good agreement with the experimental value of 51.26 eV. A similar situation is found in the calculation of the removal energy of the 1s electron from a free Li atom. When we use the LDA and LSDA formulae given by Gunnarsson and Lundqvist (1976) for this purpose, the transition-state technique yields the 1s-electron removal energies, 67.52 and 64.33 eV, for the LDA and LSDA, respectively; these values are to be compared with the experimental one of 64.39 eV (Sevier (1979)). The temperature dependence of the K-edge position obtained by the jellium–vacancy model comes only from the variation of the conduction electron density due to the thermal expansion, which is specified by the density parameter r_s. Therefore, the temperature dependence obtained by our full calculation is also essentially of the same character to that of the jellium–vacancy model, since the ion configuration around the tagged ion does not have a significant influence on the K-edge position. For the comparison of our result for the temperature dependence with the experimental one, we need the precise experimental data for the temperature dependence of the bandwidth.

4. Discussion

When a core hole is created in an ion in a liquid metal and its lifetime is sufficiently long, it produces a change in the surrounding ion distribution from $g_{II}(r)$ into $g_{IT}(r)$ as is shown in figure 1. This situation is quite different from the case of a solid metal, where the ion configuration is so rigid that such a large rearrangement of the surrounding ions does not appear even when the ionic charge of the central ion changes. It should be emphasised that our integral equation method with the aid of the transition-state technique can carry out the spectroscopic calculation by taking account of the change in the ionic distribution during an atomic process. Of particular importance is the fact that our method can give, in a self-consistent way, a pseudopotential for a tagged ion in any excited state in terms of the DCF $- C_{cT}(r)/\beta$, which yields the effective interaction between ion and excited ion from equation (24); this contrasts with the usual pseudopotential method based on a pseudopotential for an atom in the ground state. If we use the RDF $g_{II}(r)$ to describe the ion distribution around the tagged ion, $g_{IT}(r) \simeq g_{II}(r)$, even when the core hole is created and the ionic charge is changed, our method can still introduce the approximation that the relaxation effect of ions is neglected in the atomic process. When we introduce further approximations, $g_{IT}(r) \simeq \theta(r - R_{WS})$ and $\beta C_{cI}(r) \simeq Z_I e^2/r$, our formulation reduces to the treatment based on the jellium–vacancy model. The edge position of the K-edge in liquid Li is evaluated by the above three approaches, and almost the same

values, 51.36, 51.33 and 51.51 eV are obtained at 470 K, respectively; this may be attributed to the fact that the three electron distributions around the tagged ion, $g_{eT}(r)$, with $Z_T = 1.5$ exhibit a fairly good coincidence among each other as is shown in figure 2, although the ionic distributions around the tagged particle are quite different in the above three treatments. It is interesting to see that the jellium–vacancy model gives a fairly good value of the K-edge position in spite of its simple calculational procedure.

It is important for the exchange–correlation potential acting on core electrons to involve the spin polarisation effect (LSDA) instead of the LDA as table 1 exhibits; the LDA value for the K-edge position is quite different from the experimental one. Furthermore, choosing which approximation to the exchange-correlation potential should be used in the calculation is an important problem. For example, the LSDA of the Kohn–Sham form leads to a value of 50.18 eV to the K-edge position in liquid Li at 725 K, while that of the Gunnarson–Lundqvist form yields 51.67 eV; the difference between these values is greater than the variation of the K-edge when the temperature is changed from 470 to 725 K.

Already, our integral equation method, treating a liquid metal as a nucleus–electron mixture, has been proved to give the RDFs of liquid Li in excellent agreement with experimental results with the use of the atomic number as the only input (Chihara 1989). Here, it is shown that the same set of integral equations combined with the transition-state technique can give a good result for the electronic structure of an ion in liquid Li, as is examined by the comparison with the K-edge observed in the soft x-ray experiment. Thus, it is now ascertained that our integral equations can provide precisely both the liquid structure and the atomic structure of ion in a liquid metallic Li from the atomic number as the only input. A liquid metal can be thought of as one form of a high-density plasma. Therefore, our integral equations are expected to give a precise description of the ion–ion and electron–ion RDFs, as well as the atomic structure, of a high-density plasma where we have no exact knowledge except its atomic number. Also, our method can be applied to investigate the electronic structure of dissolved impurities in a liquid metal as was done by Fairlie and Greenwood (1983) for the case of Cl, F and O impurities in a Na liquid.

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