

Density of states of electrons in liquid lithium

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We present a Green-function theory for the electrons in liquid metals. In the self-energy part of the Green function, we take into account the contributions of microscopic interactions between all the particles by the GW-like approximation. The effective interelectronic potential contains the ion-static and electron-dynamic screening effects. We treat the electron-dynamical response function by the plasmon-pole approximation and the corresponding self-energy part by free-electron-plasmon coupling. The theory is applied to the liquid lithium near freezing. The calculated electron density of states is compared with experimental photoelectron spectrum. It is found that the theory is in fairly good agreement with experiment.

I. INTRODUCTION

The density of states (DOS) of electrons is of basic importance for understanding the electronic properties of the liquid metals.¹ In the earlier Green-function calculations,²⁻⁶ the ion-electron scattering was considered as the main perturbation to the free-electron system. Though the electronic screening to the ion-electron pseudopotential was taken into account, the direct interelectronic coupling was completely ignored. The DOS so predicted for liquid alkalis shows not much deviation from the free-electron model.

Recent photoemission experiments of the liquid alkalis have provided the photoelectron spectra.⁷ It is believed that the photoelectron spectrum directly reflects the actual electron DOS. In contrast to the earlier theories, the experimental results clearly exhibit strong deviations from the free-electron DOS.

Besides the Green-function calculations, the band-structure approach with local-density approximation for the liquid metals has been developed.^{1,8} On the principle of the approach, for a disordered ionic configuration, the DOS can be calculated with the density-functional techniques. The final DOS is obtained by statistical average over a number of the ionic configurations which are generated by the computer-simulation method. However, the effects of electron dynamical correlations are not taken into account in the local-density approximation. In principle, the one-electron states so obtained are not of the quasielectrons which define the DOS. For liquid lithium, the calculated DOS (Ref. 8) shows a strong enhancement at the Fermi level and the conduction bandwidth is strongly reduced compared to the free-electron model. Also, there exists obvious discrepancy between the calculation and the experiment for the photoelectron spectrum.

In this paper, we will develop a Green-function theory for the liquid metals. The self-energy part is given by the GW-like approximation.⁹ According to the Feynman diagram rule, we take into account the contributions of the interelectronic exchange correlation as well as of the electron-ion and ion-ion correlations to the self-energy.¹⁰

By so doing, the particle-plasmon coupling is involved in the electron-dynamic correlations. To simplify the calculation, we treat the dynamic electron density-density response function by the plasmon-pole approximation.¹¹ Also, we approximate the particle coupling with the plasmon by the free electron. This could not bring severe error to the final result for DOS of the main conduction band. As an example, we calculate the electron DOS for liquid lithium near freezing where the coupling constant is about $r_s = 3.3$.¹² The liquid lithium is a simple metal but the coupling is intermediate among the metals.

II. GREEN-FUNCTION FORMALISM

We consider a liquid metal consisting of ions and conduction electrons at temperature T . In most cases, the ions can be regarded as classical particles, while the electrons can be treated as degenerated fermions since the average thermal energy $k_B T$ is much less than the free-electron Fermi energy, E_F , which is determined by the electron number density n . For the sake of description, we will use the subscripts α and β to distinguish the species of particles with α (or β) = 1 for electron and 2 for ion. The interactions between the particles in q space are expressed as $v_{\alpha\beta}(q)$. The interelectronic interaction is simply given as $v_{11}(q) = 4\pi e^2/q^2$. The interionic interaction is also essentially the bare Coulomb potential since the ion core is much less than their average interdistance. The expression for the ion-electron interaction can be found in our previous paper¹² where besides the Coulomb interaction we have taken into account the exchange-correlation potential between the core electrons and the conducting electrons.

For such a liquid metal, some electronic properties can be obtained from the one-electron Green function. In this paper, we refer the Green function to the retarded Green function.¹⁰ In momentum space, it can be written as

$$G_r(k, \omega) = \frac{1}{\omega - \xi(k) - M_r(k, \omega)}, \quad (1)$$

where $\xi(k) = \hbar^2 k^2 / 2m - \mu$ is the kinetic energy of a free

electron measured from the chemical potential μ , and $M_r(k, \omega)$ is the self-energy part of the retarded Green function. The basic subject of the theory is to evaluate $M_r(k, \omega)$. Given the self-energy and thereby the Green function, the renormalized DOS can be calculated via¹

$$N(E) = -\frac{2E_F}{\hbar\pi N_c} \sum_k \text{Im}G_r(k, E), \quad (2)$$

where N_c is the total number of the conduction electrons.

It is convenient to start with the finite-temperature Green function $G(k, i\omega_n)$;¹⁰ then the real-frequency re-

tarded Green function $G_r(k, \omega)$ can be obtained by the analytic continuation $i\omega_n \rightarrow \omega + i\eta$ with η a vanishing positive quantity. According to the perturbation theory,¹⁰ the self-energy can be expanded in a series of the interactions and the Green functions. To apply the theory to a numerical calculation, one has to truncate the infinite series. The GW approximation⁹ has been shown to be successful in a number of cases.¹³ For the electrons in the liquid metals, according to the Feynman diagram rule, by GW-like approximation the self-energy can be expressed as

$$M(k, i\omega_n) = -\frac{1}{\hbar\beta V} \sum_q v_{11}(q) \sum_n e^{i\omega_n \eta} G(|\mathbf{k}-\mathbf{q}|, i\omega_n) - \frac{1}{\hbar\beta V} \sum_q \sum_{\alpha\beta} v_{1\alpha}(q) v_{1\beta}(q) \sum_m G(|\mathbf{k}-\mathbf{q}|, i\omega_n - i\nu_m) \chi_{\alpha\beta}(q, i\nu_m), \quad (3)$$

where $\beta = 1/k_B T$, V is the volume of the system, ω_n (ν_m) the Matsubara frequency for fermions (bosons), and $\chi_{\alpha\beta}(q, i\nu_m)$ represents the density-density response function between α and β species of particles. By including the local-field corrections, the response functions can be expressed in terms of the free-particle polarizabilities and the renormalized potentials.¹⁴ The first term on the right-hand side (rhs) of Eq. (3) is the exchange part in which the frequency summation gives rise to the momentum distribution function $n(|\mathbf{k}-\mathbf{q}|)$. Since the electron system is essentially degenerated, the function $n(k)$ can be derived as

$$\begin{aligned} n(k) &= \frac{1}{\hbar\beta} \sum_n e^{i\omega_n \eta} G(k, i\omega_n) \\ &= -\frac{1}{\pi} \int_{-\infty}^0 d\omega \text{Im}G_r(k, \omega). \end{aligned} \quad (4)$$

For the last term of Eq. (3), we divide the frequency summation into two parts of $\nu_m = 0$ and $\nu_m \neq 0$ terms. Those of $\nu_m \neq 0$ terms include only the contribution from the interelectronic density-density response since the ions are classical particles. By the analytic continuation $i\omega_n \rightarrow \omega + i\eta$, we have

$$\begin{aligned} M_r(k, \omega) &= -\frac{1}{V} \sum_q v_{11}(q) n(|\mathbf{k}-\mathbf{q}|) \\ &\quad - \frac{1}{V} \sum_q \phi(q) G_r(|\mathbf{k}-\mathbf{q}|, \omega) + M_0(k, \omega), \end{aligned} \quad (5a)$$

$$\begin{aligned} M_0(k, \omega) &= \frac{1}{\pi V} \sum_q v_{11}^2(q) \int_{-\infty}^0 dE [\chi_{11}(q, \omega - E) \\ &\quad \times \text{Im}G_r(|\mathbf{k}-\mathbf{q}|, E) \\ &\quad + G_r(|\mathbf{k}-\mathbf{q}|, \omega + E) \text{Im}\chi_{11}(q, E)], \end{aligned} \quad (5b)$$

where we have introduced a function

$$\phi(q) = \frac{1}{\hbar\beta} \sum_{\alpha\beta} v_{1\alpha}(q) v_{1\beta}(q) \chi_{\alpha\beta}(q, 0). \quad (6)$$

The second and last terms on the rhs of Eq. (5a) come

from the frequency summations of $\nu_m = 0$ and $\nu_m \neq 0$, respectively. To calculate the density-density response functions, we have already developed a self-consistent scheme.¹² For a description of the ionic structure factor, the scheme has been shown to be in very good agreement with experiment.

To calculate the Green function, we also need the chemical potential μ . It is determined by the electron number condition,

$$\frac{1}{E_F} \int_{-\infty}^0 dE N(E) = 1. \quad (7)$$

Equations (1), (2), (5), and (7) compose a set of integral equations. However, since $M_0(k, \omega)$ involves a three-dimensional integral, to solve the equation is almost formidable. Such difficulty has been encountered in many cases.^{11,13} A successful approximation is to treat the electronic density-density response function $\chi_{11}(q, \omega)$ by the plasmon-pole model.¹¹ According to Hedin and Lundqvist,¹¹ we have

$$v_{11}(q) \chi_{11}(q, \omega) \approx \frac{\omega_p^2}{\omega^2 - \omega_q^2}, \quad (8)$$

where $\omega_p = \sqrt{4\pi n e^2 / m}$ is the plasma frequency, and

$$\omega_q^2 = \omega_p^2 + \frac{16}{3} \omega_F^2 (q/k_F)^2 + \omega_F^2 (q/k_F)^4, \quad (9)$$

with $\omega_F = \hbar k_F^2 / 2m$ the Fermi frequency and k_F the Fermi wave number of free electrons. Furthermore, we mimic the Green functions appearing in $M_0(k, \omega)$ by their corresponding free-electron Green functions G_r^0 (not the zeroth order):

$$G_r^0(k, \omega) = \frac{1}{\omega - \xi_k^0 + i\eta}. \quad (10)$$

Here, the chemical potential in the definition of ξ_k^0 is the free electron Fermi energy $\mu_0 = E_F$. By the renormalization consideration, it is plausible to replace $\xi_k - \text{Re}M_r(k, \omega)$ with ξ_k^0 in the Green functions in the perturbation series.¹⁵ As for the particle-plasmon coupling, the plasma frequency is large enough to consider

the quasielectrons having long lifetime, $\text{Im}M_r(k, \omega) \approx 0$. By so doing, the calculation of $M_0(k, \omega)$ can be simplified as a one-dimensional integration, the same as learned by Hedin, Lundqvist, and Lundqvist for degenerated electron gas.¹¹ Knowing the particle-plasmon coupling contribution $M_0(k, \omega)$, we can solve the integral equations by iterations.

III. NUMERICAL RESULTS

To iterate the integral equations, we should first evaluate $M_0(k, \omega)$ by the aforementioned approximation scheme. For a certain momentum and frequency, the calculation of $M_0(k, \omega)$ happens to be principle integration in which the integrand contains a few points of logarithmic singularity. This requires one to pay special attention to the numerical calculation. This singularity produces discontinuity and logarithmic singularity in the function $M_0(k, \omega)$ as noticed by Hedin, Lundqvist, and Lundqvist.¹¹

By carrying out the azimuthal integration, the first term on the rhs of Eq. (5a) can be derived as a one-dimensional integral.¹⁰ We here denote this term as $M_x(k)$, referring to the exchange part of the self-energy,

$$M_x(k) = \frac{e^2}{\pi k} \int_0^\infty dq q n(q) \ln \left| \frac{k-q}{k+q} \right|, \quad (11)$$

where the integrand has a logarithmic singularity.

The second term on the rhs of Eq. (5a) is a convolution integral in q space. It can be manipulated with the Fourier transformation by which we can avoid the two-dimensional integration. The convolution can be converted to simple mathematical multiplication in the real space.

For liquid lithium at a state of $T=470$ K and $r_s=3.3$, we have previously obtained the functions $\chi_{\alpha\beta}(q, 0)$.¹² With this result, we have solved the integral equations and calculated the momentum distribution function and the DOS of the electrons. Shown in Fig. 1 are the

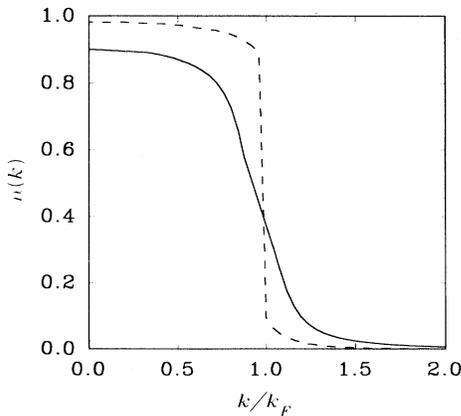


FIG. 1. Momentum distribution function $n(k)$ of the electrons in liquid lithium at $T=470$ K and $r_s=3.3$. The dashed line denotes the corresponding electron-gas result.

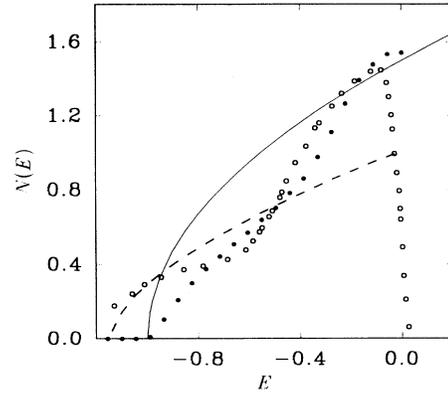


FIG. 2. Density of states $N(E)$, of the electrons in liquid lithium at $T=470$ K and $r_s=3.3$. Circles: experimental photoelectron spectrum; solid points: present calculation; dashed line: electron-gas theory (Ref. 11); solid line: free-electron model. The Fermi level is given by $E=0$.

momentum distribution functions of the present calculation and of the electron-gas theory of Hedin, Lundqvist, and Lundqvist. Due to the disordered ionic scattering, there is no clear-cut Fermi surface in the present case. In Fig. 2 we exhibit the DOS of various calculations. For comparison, we also depict the experimental photoelectron spectrum⁷ which essentially describes the DOS of the electrons. It is clear that, over the main conduction band, the present prediction is in fairly good agreement with experiment. In contrast to the free-electron parabola, the conduction band shape given by the present theory is rather triangular. The earlier Green-function calculations with pseudopotential approximations⁴⁻⁶ predicted an enhanced DOS compared to the free-electron parabola over the whole conduction band, and the enhancement increases with energy. Since we have taken into account the microscopic couplings between all the particles instead of only the ion-electron coupling with pseudopotential of the earlier theories, the present calculation gives the reasonable result.

At low energy beyond the conduction band, there appears a plasmon-electron coupling band similar in character to that predicted in the electron-gas model.¹¹ This distribution compensates for the reduction in the main conduction band.

IV. CONCLUDING REMARKS

In conclusion, we have developed the Green-function theory for liquid metals. In the electron self-energy, we have taken into account the couplings between all the particles. By applying the theory to liquid lithium near freezing, it is shown that the calculated DOS is in fairly good agreement with experiment. Since the coupling constant of the investigated system is $r_s=3.3$, the present scheme may have a wide applicability in the range from weak to this intermediate coupling for liquid metals.

For heavier liquid alkali metals, however, the coupling

constants are quite large. We do not expect the applicability of the theory to these strongly coupled systems. Some other effects may take important rule in the self-energy part of the Green function.¹ Within the present theory, instead of the free-electron-plasmon coupling, the effects of actual energy-momentum dispersion and the

finite lifetime of the quasi-electrons may be significant.² Besides the second-order terms from the density-density response contributions, the second-order exchange and higher-order terms in the self-energy may be non-negligible, and hence, a more sophisticated renormalization procedure is needed.

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