the calculated difference. These facts also lead us to the conclusion that the anisotropy of the surface is smaller than predicted.

The mass-enhancement factor for the three masses measured on the $\Gamma 5$ surface (Table II) varies from 1.20 to 1.33. As the other sheets also have enhancement factors of this order or less, we have to assume that the missing parts of the $\Gamma 5$ sheet must have a higher enhancement to account for the value 1.37 obtained by electronic specific-heat experiments.[20,21]

Note added in proof. More recent band calculations for Ir [J. Phys. F 2, 1033 (1972)] show that the Fermi-surface dimensions are very sensitive to the choice of the exchange parameter α, particularly where the d character of the bands is pronounced. These calculations also demonstrate that full Slater exchange give far better agreement with experimental results than a lower value of α; e.g., $\alpha = \frac{2}{3}$.

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Exchange and Correlation in the Electron Gas

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Recent theories of Singwi *et al.* for the dielectric response beyond the random-phase approximation are examined in the density-functional formalism. Their approximation and another from the perturbation expansion in the electron-electron interaction are used to calculate the correction to the local-density approximation of the exchange energy in atoms. The latter gives better results.

I. INTRODUCTION

Singwi and co-workers have, in a series of papers,[1–3] given approximations for the dielectric function of the electron gas beyond the random-phase approximation. Their results for the pair distribution are rather superior in that they only become slightly negative at small distances for $r_s \gtrsim 5$. The latest version by Vashishta and Singwi[3] also satisfies the compressibility sum rule in the sense that the value of the compressibility coming from the long-wavelength limit of the dielectric function agrees with the second derivative of the total energy. The most striking success of the theory is its extension to the calculation of the positron annihilation rate,[4] which agrees well with experiments for metals covering a wide range of densities.

In view of the successes of this theory, it is worthwhile to inquire closely into the nature of the approximations made. The essence of the theory is an approximate treatment of the dynamics of the particles to give an expression of the exchange and correlation part of the dielectric function in terms of the pair distribution and its density derivatives. Using the theory with the relation of the pair distribution to the imaginary part of the inverse dielectric function via the fluctuation-dissipation theorem, one has a sufficient number of equations to determine these quantities. The derivation given by Singwi *et al.*[1-3] is valid for the classical system. The status of the approximations in extending the results to a quantum-mechanical system might not seem clear at first sight. However, Schneider[5] has obtained an expression for the exchange and correlation correction close to Vashishta and Singwi's version[3] by extrapolating an expression for the compressibility of the electron gas, and which is therefore valid for the quantum system. The question remains whether there is an exact relation between the exchange and correlation part of the dielectric function and the pair-distribution function (besides the fluctuation-dissipation relation) and what approximations yield the results of Schneider and of Vashishta and Singwi from such a relation if it exists. This we wish to answer in the first part of this paper, by means of the density-functional formalism.[6,7]

Kohn and the author[7] have given a local-density approximation for the exchange and correlation potential in an inhomogeneous system which has been widely tested, and have also given a correction to the local-density approximation which has not been numerically tested. The reason is perhaps that the correction involves the knowledge of the dielectric response of the homogeneous electron gas beyond the random-phase approximation. In the second part of this work, we calculate the correction to the local-density approximation of the exchange energy in atoms. This quantity is chosen because of the relative ease of the computation and, more importantly, because of the knowledge of the exact answer, namely, the Hartree–Fock solution. For the exchange part of the dielectric response needed, we use not only the type of approximation due to Schneider and to Vashishta and Singwi, but also an approximation based on the perturbation expansion in the electron-electron interaction.

II. EXCHANGE AND CORRELATION PART OF DIELECTRIC RESPONSE

In this section, we review some facts about the dielectric function to pinpoint what we mean by the exchange and correlation part.

When the electron gas is subject to a weak perturbing potential $v(\vec{q},\omega)$ with wave vector $\vec{q}$ and frequency ω, the dielectric function $\epsilon(\vec{q},\omega)$ is defined as the ratio of the external potential to the total potential $\varphi(\vec{q},\omega)$ as seen by a test charge, i.e.,

$$\varphi(\vec{q},\omega)=v(\vec{q},\omega)/\epsilon(\vec{q},\omega)\ . \tag{2.1}$$

We define the electric susceptibility $\tilde{\chi}(\vec{q},\omega)$ as the ratio of the induced-charge density $\rho(\vec{q},\omega)$ to the *total* potential, i.e.,

$$\rho(\vec{q},\omega)=\tilde{\chi}(\vec{q},\omega)\varphi(\vec{q},\omega). \tag{2.2}$$

$\tilde{\chi}(\vec{q},\omega)$ is also known as the irreducible or proper polarization part. Since the total potential is the sum of the external potential and the electric potential due to the induced-charge density, we have

$$\epsilon(\vec{q},\omega)=1-u(\vec{q})\,\tilde{\chi}(\vec{q},\omega)\ , \tag{2.3}$$

where $u(q)$ is the Coulomb interaction between electrons,

$$u(q)=4\pi/q^2\ . \tag{2.4}$$

In the time-dependent Hartree approximation [commonly known as the random-phase approximation (RPA)],

$$\tilde{\chi}(\vec{q},\omega)\simeq\chi_0(\vec{q},\omega)\ , \tag{2.5}$$

where $\chi_0(\vec{q},\omega)$ is the density response in the noninteracting electron gas. This neglects the exchange and correlation effects in the dielectric response, which we include in the form

$$\rho(\vec{q},\omega)=\chi_0(\vec{q},\omega)\,[\varphi(\vec{q},\omega)+v_{xc}(\vec{q},\omega)]\ , \tag{2.6}$$

with

$$v_{xc}(\vec{q},\omega)=K_{xc}(\vec{q},\omega)\,\rho(\vec{q},\omega)\ . \tag{2.7}$$

Then, by Eq. (2.2),

$$\tilde{\chi}(\vec{q},\omega)=\chi_0(\vec{q},\omega)/[1-K_{xc}(\vec{q},\omega)\chi_0(\vec{q},\omega)]\ . \tag{2.8}$$

We may simply regard the introduction of v_{xc} and K_{xc} as a convenient way of defining the difference between the exact susceptibility and the RPA. However, v_{xc} may be interpreted as the local field acting on the induced-charge density owing to electron exchange and correlation.[2,8] Although the form for the susceptibility, (2.8), may seem somewhat unnatural from the viewpoint of the conventional diagrammatic expansion, it arises in a natural way both from the approach of Singwi *et al.*[1-3] and from our approach by means of the density-functional formalism, as we shall see presently.

By the nature of the density-functional formalism, we shall only be able to consider the static response, i.e., $K_{xc}(\vec{q},0)$, and henceforth omit the $\omega=0$ designation for all static responses. Singwi *et al.* have used for the frequency-dependent dielectric function the static approximation

$$K_{xc}(\vec{q}, \omega) \simeq K_{xc}(\vec{q}) \ . \qquad (2.9)$$

A static external potential $v(\vec{r})$ of any magnitude applied to the interacting electron gas will produce a density distribution $n(\vec{r})$ for the ground state. Hohenberg and Kohn[6] have shown that the ground-state energy can be written in the form

$$E = \int d\vec{r}\, v(\vec{r})\, n(\vec{r}) + \tfrac{1}{2} \int d\vec{r} \int d\vec{r}\,' n(\vec{r}) \times u(\vec{r} - \vec{r}\,')\, n(\vec{r}\,') + F[n] \ , \qquad (2.10)$$

where $F[n]$ denotes a quantity completely determined by the knowledge of the density distribution. Kohn and the author[7] noted that by writing

$$F[n] = T_s[n] + E_{xc}[n] \ , \qquad (2.11)$$

where $T_s[n]$ is the kinetic energy of a noninteracting system, it can be proved that the density distribution can be determined exactly from a one-particle Schrödinger equation with a self-consistent potential

$$v(\vec{r}) + \int d\vec{r}\,' \, u(\vec{r} - \vec{r}\,')\, n(\vec{r}\,') + v_{xc}[\vec{r}\, ; n] \ , \qquad (2.12)$$

where

$$v_{xc}[\vec{r}; n] = \delta E_{xc}[n] / \delta n(\vec{r}) \ . \qquad (2.13)$$

Let us now relate the dielectric response to the density functionals. For the linear response, treat $v(\vec{r})$ as weak; this produces the density

$$n(\vec{r}) = n_0 + \delta n(\vec{r}) \ , \qquad (2.14)$$

with $\delta n(\vec{r})$ being small fluctuations about the mean n_0. Expand the terms in the total energy in powers of $\delta n(\vec{r})$, yielding[6]

$$T_s[n] = T_s(n_0) + \tfrac{1}{2} \int d\vec{r} \int d\vec{r}\,' \delta n(\vec{r}) \times K_0(\vec{r} - \vec{r}\,'; n_0)\, \delta n(\vec{r}\,') + \cdots \qquad (2.15)$$

and

$$E_{xc}[n] = E_{xc}(n_0) + \tfrac{1}{2} \int d\vec{r} \int d\vec{r}\,' \delta n(\vec{r}) \times K_{xc}(\vec{r} - \vec{r}\,'; n_0)\, \delta n(\vec{r}\,') + \cdots \ . \qquad (2.16)$$

By comparing the second-order term in energy expressed in terms of the perturbation $v(\vec{r})$ with energy in terms of the induced density, one can readily see that[6,7]

$$K_0(\vec{q}) = -1/\chi_0(\vec{q}) \ , \qquad (2.17)$$

where we denote the Fourier transform simply by changing the variable from $\vec{r}$ to $\vec{q}$, and $K_{xc}(\vec{r})$ defined in Eq. (2.16) is just the Fourier transform of the $K_{xc}(\vec{q})$ in Eq. (2.8).

Alternatively, by the variational theorem[6] of the energy, in Eq. (2.10), with respect to the density, one obtains to order linear in the perturbation

$$v(\vec{q}) + u(\vec{q})\, \delta n(\vec{q}) + \{K_0(\vec{q}) + K_{xc}(\vec{q})\}\, \delta n(\vec{q}) = 0 \qquad (2.18)$$

from which, again, Eqs. (2.17) and (2.8) follow. It shows that for the static case, the potential v_{xc} introduced in Eq. (2.6) is the exchange and correlation potential in the sense of Eqs. (2.12) and (2.13).[7]

In summary, we have given a somewhat long-winded demonstration that the exchange and correlation correction to the RPA for the dielectric function in the form of Eq. (2.8) is, in the static case, simply given by

$$K_{xc}(\vec{r} - \vec{r}\,') = \left.\frac{\delta^2 E_{xc}[n]}{\delta n(\vec{r})\, \delta n(\vec{r}\,')}\right|_{n(\vec{r}) = n_0 = n(\vec{r}\,')} \ . \qquad (2.19)$$

III. DIELECTRIC FUNCTION IN TERMS OF PAIR-DISTRIBUTION FUNCTION

In Ref. 7, we attempted to construct the functional $E_{xc}[n]$ with the assumed knowledge of the linear response $K_{xc}(\vec{r})$of the homogeneous electron gas. Here we reverse the procedure and use relation (2.19) to find the dielectric response of the homogeneous gas, assuming a knowledge of the energy functional for a general inhomogeneous electron system.

From the definition (2.10), the energy term $F[n]$ is given by[6]

$$F[n] = \int d\vec{r} \frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial\vec{r} \cdot \partial\vec{r}\,'}\, n_1(\vec{r}, \vec{r}\,') \right)_{\vec{r} = \vec{r}\,'} + \tfrac{1}{2} \int d\vec{r} \int d\vec{r}\,' u(\vec{r} - \vec{r}\,')\, C_2(\vec{r}, \vec{r}\,') \ . \qquad (3.1)$$

The first term is the kinetic energy and the second is the potential energy minus the electrostatic contribution given by the first two terms on the right-hand side of Eq. (2.8). Here, $n_1(\vec{r}, \vec{r}\,')$ is the one-particle density matrix and $C_2(\vec{r}, \vec{r}\,')$ is the two-particle correlation function, related to the two-particle density matrix by

$$C_2(\vec{r}, \vec{r}\,') = n_2(\vec{r}, \vec{r}\,';\, \vec{r}, \vec{r}\,') - n(\vec{r})\, n(\vec{r}\,') \ . \qquad (3.2)$$

We define the pair-distribution function in the inhomogeneous gas by

$$n_2(\vec{r}, \vec{r}\,';\, \vec{r}, \vec{r}\,') = n(\vec{r})\, g[\vec{r}, \vec{r}\,'; n]\, n(\vec{r}\,') \ . \qquad (3.3)$$

Since it has been shown[6] that the external potential $v(\vec{r})$ is a functional of the density $n(\vec{r})$, all properties, including the pair-distribution function, are functionals of $n(\vec{r})$. In Eq. (3.3), the density dependence is emphasized.

The second term on the right-hand side of Eq. (3.1) gives what may be termed the "potential-energy part" of the exchange and correlation energy $E_{xc}[n]$, and with the help of Eq. (3.3) can be written as

$$U_{xc}[n] = \tfrac{1}{2} \int d\vec{r} \int d\vec{r}\,' n(\vec{r})\, u(\vec{r} - \vec{r}\,') \times \{g[\vec{r}, \vec{r}\,'; n] - 1\}\, n(\vec{r}\,') \ . \qquad (3.4)$$

The "kinetic-energy part" of the exchange and correlation energy $E_{xc}[n]$ is the difference between the first term on the right-hand side of Eq. (3.1) and the kinetic energy of the noninteracting system $T_s[n]$. Let us write it in the form

$$T_{xc}[n]=\tfrac{1}{2}\int d\vec{r}\int d\vec{r}\,'n(\vec{r})u(\vec{r}-\vec{r}\,')h[\vec{r},\vec{r}\,';n]n(\vec{r}\,') , \qquad (3.5)$$

and $h[r, r';n]$ may loosely be termed the "kinetic pair distribution."

Hence, the exchange and correlation energy can be written in the same form,

$$E_{xc}[n]=\tfrac{1}{2}\int d\vec{r}\int d\vec{r}\,'n(\vec{r})u(\vec{r}-\vec{r}\,') \times\{j[\vec{r},\vec{r}\,';n]-1\}n(\vec{r}\,') , \qquad (3.6)$$

where, from Eqs. (3.4) and (3.5),

$$j=g+h . \qquad (3.7)$$

By Eq. (2.19), we obtain the exchange and correlation correction to the dielectric function

$$\begin{aligned}K_{xc}(\vec{r}-\vec{r}\,')&=u(\vec{r}-\vec{r}\,')\{j[\vec{r}-\vec{r}\,';n]-1\}\\&+2\int d\vec{r}_1 n\frac{\delta j[\vec{r},\vec{r}_1;n]}{\delta n(\vec{r}\,')}u(\vec{r}-\vec{r}_1)\\&+\tfrac{1}{2}n^2\int d\vec{r}_1\int d\vec{r}_2\frac{\delta^2 j[\vec{r}_1\cdot\vec{r}_2;n]}{\delta n(\vec{r})\,\delta n(\vec{r}\,')}u(\vec{r}_1-\vec{r}_2) , \qquad (3.8)\end{aligned}$$

where the quantities on the right-hand side are evaluated for the homogeneous system, i.e., $n(\vec{r}) = \text{const}$.

Although this formula is exact, it is only useful if we can construct the pair-distribution function $j[\vec{r}, \vec{r}\,';n]$. At present, we have no satisfactory theory for that. However, a few crude approximations will give us formulas very close to those of Singwi and co-workers.[1-3]

From Eq. (3.8), if we neglect the kinetic correlation as well as the density dependence of the pair-distribution function, we obtain the approximation

$$K_{xc}(\vec{r})\simeq u(\vec{r})\{g(\vec{r})-1\} , \qquad (3.9)$$

which is close to the result in Ref. 1,

$$\nabla K_{xc}(\vec{r})\simeq\{g(\vec{r})-1\}\nabla u(\vec{r}) . \qquad (3.10)$$

The reason for the difference of a gradient will be explained later. Looking at the approximation this way, it is clear why the compressibility sum rule is not satisfied.

The version in Ref. 2 gives the approximation of the same form as Eq. (3.10) except that the Coulomb interaction $u(\vec{r})$ is screened by the dielectric function. This is unjustifiable from Eq. (3.8) and also physically unreasonable, since the screening has already been accounted for in large measure by the exchange and correlation hole provided by the pair-distribution function.

The results of Schneider[5] and of Vashishta and Singwi[3] are of the form

$$\nabla K_{xc}(\vec{r})\simeq\left(1+an\frac{\partial}{\partial n}\right)\{g(\vec{r};n)-1\}\nabla u(\vec{r}) . \qquad (3.11)$$

Schneider neglected the kinetic correlation and obtained the value $a=\frac{1}{2}$. Vashishta and Singwi used the parameter a to simulate the effect of kinetic correlation and found an optimum value of $\frac{2}{3}$ for the whole range of metallic densities.

An approximation comparable to the last version can be obtained from Eq. (3.8) by using the pair-distribution functions at constant density before density differentiation, i.e.,

$$\left.\frac{\delta j[\vec{r},\vec{r}_1;n]}{\delta n(\vec{r}\,')}\right|_{n(\vec{r})=n}\simeq\frac{\partial j(\vec{r}-\vec{r}\,';n)}{\partial n}\delta(r_1-r') , \qquad (3.12)$$

$$\left.\frac{\delta^2 j[\vec{r}_1,\vec{r}_2;n]}{\delta n(\vec{r})\,\delta n(\vec{r}\,')}\right|_{n(\vec{r})=n}\simeq\frac{\partial^2 j(\vec{r}-\vec{r}\,';n)}{\partial n^2}\delta(\vec{r}_1-\vec{r})\,\delta(\vec{r}_2-\vec{r}\,') , \qquad (3.13)$$

where $j(\vec{r};n)$ denotes the pair-distribution function for the homogeneous electron gas at density n. Then,

$$K_{xc}(\vec{r})\simeq u(\vec{r})\left(1+2n\frac{\partial}{\partial n}+\tfrac{1}{2}n^2\frac{\partial^2}{\partial n^2}\right)\{j(\vec{r};n)-1\} . \qquad 3.14)$$

The cause of the differences of a position gradient and density derivatives between the two formulas (3.11) and (3.14) is easily understood by comparing Schneider's derivation with ours. He took the energy expression for the homogeneous electron gas, differentiated twice with respect to the density, and fixed the $q=0$ form of K_{xc} by appealing to the compressibility sum rule. However, on the first density derivative, he used the virial theorem with the potential energy in the form of $-\vec{r}\cdot\nabla u(\vec{r})$. Had he used the equivalent form of $u(r)$, he would have obtained a formula without the gradient operator. The remaining difference in the density derivative is due to the use of the virial theorem for the homogeneous gas, which is equivalent to replacing $1+n\partial/\partial n$ by $\frac{1}{3}$.

Equation (3.14) is still not a relation between K_{xc} and the static pair-distribution function $g(\vec{r})$ unless we can construct $h(\vec{r})$. Vashishta and Singwi's[3] parametrization is one way. Alternatively, within the spirit of the Singwi-type approximation, we assume that the virial theorem[9] which relates the kinetic and potential part of the exchange and correlation energy of the free-electron gas can be extended to h and g and calculate h as a density integral of g.

By construction, it is clear that Eq. (3.14) satisfies the compressibility sum rule. If we neglect correlation but keep exchange, the small r (or, equivalently, large q) values of $K_x(\mathrm{r})$ for both approximations (3.11) and (3.14) are the same, since $g(r)$ tends to $\frac{1}{2}$ for small r at any density in the Hartree-Fock approximation. However, in the next section, we shall see some differences in the two approximations. It is of some interest to repeat the calculations carried out by Vashishta and Singwi with Eq. (3.14) to compare with their results for the properties of the electron gas.

IV. GRADIENT CORRECTION TO EXCHANGE ENERGY IN ATOMS

In the local-density approximation,[7] the exchange and correlation energy is

$$E_{xc}[n] \simeq \int d\vec{r}\, n(\vec{r})\, \epsilon_{xc}(n(\vec{r})) \,, \qquad (4.1)$$

where $\epsilon_{xc}(n)$ is the exchange and correlation energy per electron in the homogeneous electron gas with density n. This approximation has been widely used in atoms and solids. The most widely used correction to this approximation is simply to multiply $\epsilon_x(n)$ by an adjustable parameter, known as the $X\alpha$ method. However, one may regard, Eq. (4.1) as the leading term in the gradient expansion. Herman *et al.*[10] were the first to show that the difference between the Hartree–Fock energy in atoms and the local-density approximation can be fully accounted for by the next-order-gradient term with an adjustable coefficient which varies very little from atom to atom. The coefficient of the gradient term, for the exchange only, can be calculated from first principles[11,12] and is only about one-third to one-fifth as big as the adjusted value of Herman *et al.*[10] Ortenburger and Herman[12] argued that the discrepancy represented the effects of the higher-order-gradient terms. The second-order-gradient term to the correlation energy in atoms is found by Ma and Brueckner[13] to be much too large.

In view of the experiences with the gradient term corrections above, as well as the gradient term corrections to the Thomas–Fermi approximation, it appears that term-by-term calculations of the gradient series will not necessarily give successively improved answers. Kohn and the author[7] have suggested a correction to the local-density approximation, given by

$$\Delta E_{xc}[n] \simeq -\tfrac{1}{4}\int d\vec{r}\int d\vec{r}\,'\, K_{xc}(\vec{r}-\vec{r}\,'\,;\, n(\tfrac{1}{2}\vec{r}+\tfrac{1}{2}\vec{r}\,'))$$
$$\times\{n(\vec{r})-n(\vec{r}\,')\}^2 \,. \qquad (4.2)$$

This is the sum of a subseries of the gradient expansion[6] involving all terms of type $\nabla^{2l-m}n\,\nabla^m n$. $K_{xc}(r, n)$ is just the exchange and correlation part of the dielectric response defined in Eqs. (2.19), (2.16), or (2.8). Neglected in this correction are terms involving more than two factors of density derivatives. Their summation would involve nonlinear-response functions of the homogeneous electron gas.

In this section, we report the calculations of the correction to the local-density approximation of only the exchange energy in atoms, using Eq. (4.2), for the reasons given in the Introduction. Three approximations for the exchange part of the dielectric response, $K_x(r\,;n)$, are used: (a) the Schneider–Vashishta–Singwi approximation given by Eq. (3.11), with $a=\frac{1}{2}$ and the pair-distribution function appropriate to the electron gas in the Hartree–Fock approximation, (b) the related approximation (3.14) derived in this paper, with $j(r\,;n)$ again given by $g(r\,;n)$ in the Hartree–Fock approximation, and (c) an approximation of the expansion of the Hartree–Fock susceptibility $\tilde{\chi}$ in powers of e^2,

$$\tilde{\chi} = \chi_0 + \tilde{\chi}_1 + \cdots \,, \qquad (4.3)$$

giving

$$K_x(q) = \tilde{\chi}_1(q)/[\chi_0(q)]^2 \,, \qquad (4.4)$$

if we approximate the higher-order terms in the series (4.3) by the geometric progression starting with the first two terms. The quantity $\tilde{\chi}_1(\vec{q})$ has been computed by Geldart and Taylor,[14] and their values are used here.

Note that all three approximations satisfy the compressibility sum rule, i.e., in the Hartree–Fock approximation,

$$K(q=0) = -\pi e^2/k_F^2 \,. \qquad (4.5)$$

Only approximation (c) gives the correct q^2 term.[11] For large q, (a) and (b) give

$$K_x(q) \sim -\tfrac{1}{2}u(q) \,, \qquad (4.6)$$

but (c) gives the correct Hartree–Fock value of

$$K_x(q) \sim -\tfrac{1}{3}u(q) \,. \qquad (4.7)$$

Unlike the second-order gradient term,[10] $K_x(q)$ used in Eq. (4.2) tends to zero for large gradients. The density for $K_x(\vec{r}-\vec{r}\,'\,;n)$ is chosen for the spherical atoms at the mean radius $\frac{1}{2}(r+r')$ rather than the midpoint.

The results for various inert-gas atoms are shown in Table I. It is convenient to use analytical formulas for the density which have been fitted to the Hartree–Fock solution[15] rather than the numerical solution in the local-density approximation.[16] Because of the variational theorem,[6] the difference for the energy calculations is not important, as is borne out by the rows in Table I marked E_x(TS), using Eq. (4.1) and the analytical

TABLE I. Exchange energies in atoms. The quantities in each row are explained in the text. Energy in units of Ry.

	He	Ne	Ar	Kr
E_x(TS)	−1.707	−21.873	−55.551	
E_x	−1.768	−22.032	−55.632	−177.498
ΔE_x	−0.275	−2.115	−4.607	−10.423
a	0.195	1.584	3.350	7.974
b	−0.004	−0.177	−0.439	−1.216
c	−0.212	−1.284	−1.672	−5.993

expression for the density. ΔE_x is the difference between the Hartree–Fock energy and the local-density approximation using exchange without correlation, taken from Ref. 16. The last three rows are the corrections to the local-density approximation ΔE_x, using Eq. (4.2) and the approximations for K_x described above.

The Schneider–Vashishta–Singwi (SVS) response gives the wrong sign for ΔE_x. This is because their $K_x(q)$ is quite close to the Hubbard form,[1] which is always negative and monotonically increasing to zero as q increases, thus always giving a positive value to ΔE_x as is evident from Eq. (4.2). Equation (4.4), the perturbation approximation, on the other hand, decreases first as q increases from zero. See Fig. 1, where this is plotted and contrasted with the Hubbard approximation

$$K_x(q) \simeq -2\pi e^2/(q^2+2k_F^2)\,, \tag{4.8}$$

with the term $2k_F^2$ chosen to fit the compressibility sum rule. This negative curvature in version (c) is picked out by the density factor in Eq. (4.2) and appears to be essential here for giving the correct sign to ΔE_x. Version (b), though it gives the correct sign for ΔE_x, yields values which are much too small. Thus, Eq. (3.14) appears to give slightly better q dependence than SVS, but not much better.

The results in Table I show that version (c) gives the best approximation for $K_x(q)$, the exchange part of the response beyond RPA. We conjecture that the remaining 40–50% error in ΔE_x is likely, mainly due to the approximation in Eq. (4.2) where products of more than two density derivatives are mostly neglected. The Singwi-type approximation is sufficiently good for large q to explain the electron-electron and electron-positron correlations at short distances and is made to obey the compressibility sum rule (i.e., correct at $q=0$), but not necessarily good at small or finite q values. For properties such as ΔE_x which are sensitive to q^2 and higher-order terms in the response, it is important to take into account the functional dependence of the pair-distribution function on the density distribution in the slightly inhomogeneous system; i.e., approximations (3.12) and (3.13) are probably inadequate. However, we should emphasize that only the exchange part has been tested. It remains to be seen whether the Singwi-type approximation for the combined exchange and correlation term $K_{xc}(q)$ gives a better q dependence.

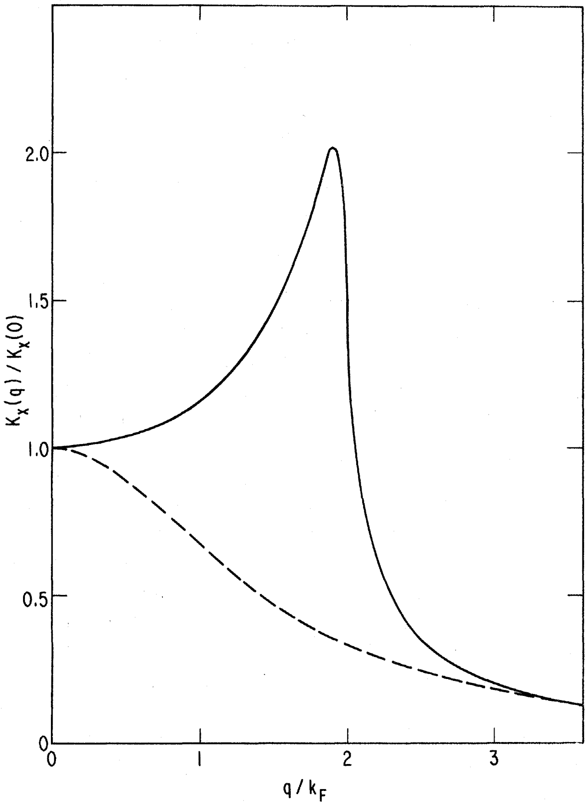

FIG. 1. Exchange part of the response from the perturbation theory (solid line), Eq. (4.4), and from the Hubbard form (dashed line), Eq. (4.8).

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Comparison of the Isotope Effect for Diffusion of Sodium and Silver in Lithium*

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Separate measurements were made at 150 °C of the simultaneous diffusion of sodium isotopes (^{22}Na and ^{24}Na) and silver isotopes (^{105}Ag and ^{110m}Ag) in lithium. The strength of the isotope effect $f\Delta K$ for sodium is 0.19 ± 0.01 and for silver 0.26 ± 0.01. These values do not correlate well with recent calculations of ΔK determined for impurity diffusion on the basis of the dynamical theory of diffusion. Measurement of the diffusion of silver in lithium is 45% greater than earlier data, and a possible explanation for this discrepancy is given.

I. INTRODUCTION

Many measurements of the isotope effect in diffusion have been made in the past ten years because of the information they provide on the basic mechanism of diffusion in crystals. The interpretation of these measurements has not always been unambiguous, and clarification has been sought using two distinct theories. However, both the reaction-rate theory[1-3] and the dynamical theory[4-6] result in an equation for the isotope effect of the same general form. The equation is given by

$$\frac{D_\alpha}{D_\beta} - 1 = f\Delta K\left[\left(\frac{m_\beta}{m_\alpha}\right)^{1/2} - 1\right] , \qquad (1)$$

where D_α, m_α, D_β, and m_β refer to the diffusion coefficient and mass of α and β isotope, respectively. f is the correlation factor and ΔK is interpreted in reaction-rate theory as that fraction of the total translational kinetic energy associated with the decomposition of the saddle-point configuration possessed by the migrating atom.

For self-diffusion in cubic metals, f is a geometric factor dependent only on the crystal structure and the atomic-jump process. Measurements of D_α/D_β yield the product $f\Delta K$; thus, if ΔK is close to unity, the experimental results yield an unambiguous value of f, which serves to identify the diffusion mechanism. Measurements of the isotope effect in metals with a close-packed structure[7-15] have shown that diffusion occurs primarily by means of vacancies. Measurements of the isotope effect in body-centered-cubic (bcc) metals[14-18] have yielded such low values of the isotope effect that it was impossible to identify, unambiguously, the mechanism of diffusion. However, experimental evidence does indicate, from measurements of the macroscopic change of length and the x-ray lattice parameter as a function temperature, that in lithium[19] and also in sodium[20] above room temperature, vacancies are the predominant defect. The measurements of the enhancement of sodium self-diffusion by additions of potassium[21] also suggest a vacancy mechanism of diffusion.

The low values of the isotope effect were found in self-diffusion experiments in which f is a geometric factor, and so a theoretical justification was sought for a low value of ΔK. Calculations of ΔK based on both reaction-rate theory[22,23] and dynamical theory[5] gave values of ΔK within 20% of unity. This similarity was unexpected because in the calculation of ΔK the differences in the theories should show most clearly.[22] In seeking to determine the relative merits of each theory, Achar[24] has developed, from the dynamical theory, the effect of resonance and local modes on ΔK. The theory is based on the fact that an impurity with mass much greater than that of the lattice atoms will give rise to resonance modes, whereas impurities of mass similar to the lattice atoms will give rise to localized modes. The effect of these modes on ΔK has shown that ΔK has a marked dependence on the mass factor M'/M, where M' is the impurity mass and M is the mass of a host atom. The extent to which ΔK will change is, of course, governed experimentally by the relative magnitudes of M' and M. Achar has calculated values of ΔK for three host lattices: lithium, sodium, and aluminum.

The effect of impurity mass on the value of ΔK has also been determined from the dynamical theory in a recent paper by Feit.[25] In Feit's approach, the resonance modes are not treated explicity, and the variation of ΔK is determined relative to ΔK_0. Feit used experimental values of ΔK_0 and suggested that the greatest differences in $\Delta K/\Delta K_0$ would be seen where ΔK_0 is low, as in sodium.