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Universal behavior of exchange-correlation energy in electron-hole liquid

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Exchange-correlation energy of electron-hole liquid (EHL) is shown to be independent of different band characteristics of semiconductors. A simple expression of $\epsilon_{\rm xc}$ for EHL in all semiconductors is given. In units of excitonic rydberg, $\epsilon_{\rm xc}=(a+br_s)/(c+dr_s+r_s^2)$, where $a=-4.8316$, $b=-5.0879$, $c=0.0152$, and $d=3.0426$. Ground-state and thermodynamic properties calculated with this expression are in good agreement with earlier theoretical calculations and experimental results.

Exchange-correlation energy is a central quantity in the determination of ground-state, thermodynamic, and surface properties of electron-hole liquid (EHL). The Hartree-Fock (HF) energy, which is the expectation value of kinetic and potential energies with respect to the Slater determinant, can be exactly evaluated including such diverse band-structure effects as the valley degeneracy, anisotropy of bands, valence-band coupling and warping.[1-3] In most semiconductors EHL is not bound in HF approximation,[4] and it is the correlation contribution which makes EHL a stable phase. The complex band-structure effects are difficult to incorporate in the correlation energy, and therefore it is usually evaluated in simplified models of semiconductors where most of the band-structure effects are ignored.

The ground-state energy for an uniform EHL can be written as

$$\epsilon=t_k+\epsilon_{\rm xc}\ , \tag{1}$$

where t_k is the noninteracting kinetic energy. The exchange-correlation energy $\epsilon_{\rm xc}$ is an integral of the interaction energy over the interaction strength:

$$\epsilon_{\rm xc}=\int_0^{e^2}\frac{d\lambda}{\lambda}E_{\rm int}(\lambda)\ . \tag{2}$$

Because exchange and correlation are parts of the same interaction energy, they should be treated in exactly the same model for the band structure of a semiconductor. By this we mean that if, for example, the conduction-band anisotropy is ignored in correlation energy, it should also be left out in exchange. While band characteristics can greatly affect exchange and correlation energies separately, the effects on correlation are opposite to those on exchange. In reduced units, the sum of exchange and correlation energies is almost independent of band characteristics and it depends on r_s alone. In what follows we shall demonstrate that $\epsilon_{\rm xc}$ is insensitive to band parameters of semiconductors.

EFFECT OF VALLEY DEGENERACY

Consider EHL in a semiconductor like Ge, which has four conduction bands and two valence bands, and is therefore denoted by Ge(4;2).[5] To study the effect of valley degeneracy, we shall replace the four conduction bands by a variable number ν_e, and denote the new system by Ge(ν_e;2). As regards the band structure of Ge(ν_e;2) the following simplifications are made: The anisotropic conduction bands are replaced by isotropic bands, and the valence bands are represented by two identical, isotropic, degenerate bands without valence-band coupling.[2,3] In this model of Ge(ν_e;2), the exchange energy per e-h pair is given in units of Ry by,

$$\epsilon_x=-\frac{0.9163}{r_s}(\nu_e^{-1/3}+2^{-1/3})\ , \tag{3}$$

where 1 Ry$=e^2/2\kappa a_{\rm ex}$, and $a_{\rm ex}$ is excitonic Bohr radius. To investigate the effect of ν_e on exchange and correlation it is essential that they are evaluated in exactly the same model of the band structure. The correlation energy of EHL in Ge(ν_e;2) is evaluated for a number of values of ν_e in fully self-consistent (FSC) approximation.[6] The dependence of ϵ_x, ϵ_c, and $\epsilon_{\rm xc}$ on ν_e at $r_s=1$ is shown in Fig. 1(a). While the magnitude of ϵ_x decreases with ν_e, the magnitude of correlation energy increases. The decrease in exchange is nearly the same as the increase in correlation, and *the sum* $\epsilon_{\rm xc}$ *is therefore nearly independent of* ν_e. This near independence of $\epsilon_{\rm xc}$ holds not just at $r_s=1$, but for a

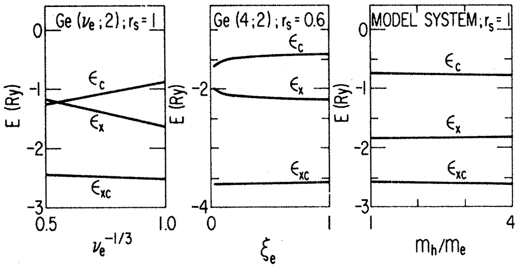

FIG. 1. Variations of exchange energy ϵ_x, correlation energy ϵ_c, and their sum, ϵ_{xc}, per e-h pair with (a) number of degenerate conduction bands ν_e (b) conduction-band anisotropy $\xi = m_{et}/m_{el}$, where m_{et} and m_{el} are, respectively, the transverse and longitudinal masses, and (c) hole to electron mass ratio. The energies are measured in units of excitonic rydberg, 1 Ry$=e^2/2\kappa a_{ex}$, where a_{ex} is excitonic Bohr radius.

wide range of r_s values. A simple explanation of this is that the main contribution to ϵ_{xc} comes from plasmons whose energy, $\hbar\omega_p = (12/r_s^3)^{1/2}$ Ry, depends only on r_s and not on the number of valleys in which electrons and holes reside. The weak variation of ϵ_{xc} with ν_e is a general feature; to a lesser degree it is also present in random-phase (RPA) and Hubbard approximations (HA).

EFFECT OF ANISOTROPY

To study the effect of anisotropy, the conduction bands in Ge(4;2) are taken to be ellipsoids with varying ratio ξ_e of transverse (m_{et}) to longitudinal masses (m_{el}) or electrons. The exchange energy per e-h pair can be written as

$$\epsilon_x = -\frac{0.9163}{r_s}[4^{-1/3}\phi(\xi_e)+2^{-1/3}] , \qquad (4)$$

again in units of Ry, where $\phi(\xi_e)$ is a measure of the effect of anisotropy.[3] The correlation energy of the system is evaluated in Hubbard approximation. Figure 1(b) shows the dependence of ϵ_x, ϵ_c, and ϵ_{xc} on ξ_e. The curves for ϵ_x and ϵ_c are nearly straight lines except when ξ_e is very small; close to $\xi_e = 0$ the exchange and correlation energies exhibit nearly equal but opposite curvatures, and *the sum* ϵ_{xc} *is therefore insensitive to any variations in* ξ_e. For anisotropic bands, the evaluation of ϵ_c in FSC approximation[6] is considerably more difficult than in Hubbard approximation.

EFFECT OF ELECTRON-HOLE MASS RATIO

To investigate the effect of electron-hole mass ratio, consider a model system with a single isotropic conduction band of mass m_e and an isotropic valence band of mass m_h. The exchange energy is independent of the mass ratio. Figure 1(c) shows the dependence of ϵ_c in FSC approximation on the ratio m_h/m_e at $r_s = 1$. *Since* ϵ_c *is nearly flat and the variation in* ϵ_{xc} *is a result of variation in* ϵ_c *alone, the exchange and correlation energy curve is flat too.* The variation of ϵ_c with the mass ratio is substantially greater in RPA,[6] while in HA the change in ϵ_c is less than RPA, but still greater than FSC approximation.

Other band characteristics which affect exchange and correlation are valence-band coupling (VBC) and warping of hole bands. In Ge and Si, the effect of VBC on exchange energy[3] is given by a function ψ which has a value $1/2^{1/3} = 0.7937$ when the valence bands are represented by two identical, isotropic, degenerate bands. In the presence of VBC, the value of ψ in Ge(4;2) is 0.726.[3] In exchange energy the effect of VBC is therefore equivalent to an increase in number of bands, which increases the magnitude of ϵ_c. We therefore feel that the sum of exchange and correlation will be perhaps insensitive to valence-band coupling. Carrying this argument to the case of valence-band warping, we expect its effect on ϵ_x and ϵ_c to be opposite and therefore the sum ϵ_{xc} will be a weak function of warping.

GENERAL EXPRESSION FOR ϵ_{xc}

It is worth reiterating that exchange and correlation effects should be treated on equal footing; if a certain band-structure effect is ignored in correlation energy, it should also be excluded in exchange, since the inclusion of a given band characteristic in exchange is canceled to a large extent by the corresponding contribution to correlation. In reduced units the sum of exchange and correlation energies is nearly free from the effects of band structure and depends only on r_s. Over a wide range of r_s values, ϵ_{xc} can be fitted to the following simple form (in units of Ry):

$$\epsilon_{xc}(r_s) = \frac{a + br_s}{c + dr_s + r_s^2} , \qquad (5)$$

where $a = -4.8316$, $b = -5.0879$, $c = 0.0152$, and $d = 3.0426$. A plot of ϵ_{xc} vs r_s is shown in Fig. 2. For comparison FSC values of ϵ_{xc} in Si(6;2),

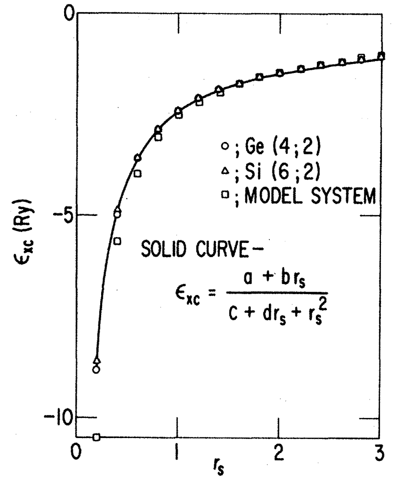

FIG. 2. Exchange-correlation energy ϵ_{xc} in units of excitonic rydberg as a function of dimensionless variable r_s in Ge(4;2), Si(6;2), and the model system consisting of a simple isotropic conduction band and an isotropic valence band, The solid curve is the fit to ϵ_{xc} by the expression given in the figure with $a=-4.8316$, $b=-5.0879$, $c=0.0152$, and $d=3.0426$.

Ge(4;2), and the model system are also shown in Fig. 2. It is clear that the above expression provides an excellent fit to the numerical values of ϵ_{xc} in all systems. A simple expression like Eq. (5) tremendously facilitates the evaluation of the energetics of EHL. Given ϵ_{xc}, one needs only to evaluate the noninteracting kinetic energy of EHL; the ground-state, thermodynamic, and surface properties can then be calculated in a straightforward manner.

In many systems the kinetic energy per e-h pair can be written as α/r_s^2, where α contains band-structure effects.[7] Using ϵ_{xc} from Eq. (5), the total energy in Ry per e-h pair can be written as

$$\epsilon=\frac{\alpha}{r_s^2}+\frac{a+br_s}{c+dr_s+r_s^2}\ . \tag{6}$$

The minimum of ϵ gives the ground-state energy ϵ_0 and the equilibrium r_0 in the liquid phase; the binding energy of EHL is the difference between ϵ_0 and the excitonic binding energy.

The compressibility χ can be easily obtained from

$$\chi^{-1}=n_0^3\frac{\partial^2\epsilon_0}{\partial n_0^2}\equiv\frac{1}{12\pi a_{ex}^3}\frac{1}{r_0}\left[\frac{\partial^2\epsilon}{\partial r_s^2}\right]_{r_s=r_0}\ . \tag{7}$$

The thermodynamic properties of EHL in the plasma model[1,8,9] can be easily calculated using the general expression expression for ϵ_{xc}. In Ge, Si, and several other systems we find that the coefficients of T^2 in the low-temperature expansion of density, chemical potential, and Fermi energy are in good agreement with experimental[8] and earlier theoretical results.[9] The evaluations of critical density n_c the temperature T_c are also straightforward.

The ratio of critical density to equilibrium density at $T=0$ K can be written as

TABLE I. Results for various properties of EHL in a number of semiconductors using the general expression of ϵ_{xc} given in Eq. (5). Notations for different quantities are: equilibrium $r_s(r_0)$, ground-state energy per e-h pair (ϵ_0), critical $r_s(r_c)$, critical temperature (T_C), compressibility (χ), and coefficients of T^2 terms in low-temperature expansions of density n, chemical potential μ_F, and Fermi energy E_F. The coefficients δn, $\delta\mu$, and δE_F are defined through $n(T)=n(0)[1-\delta nT^2]$, $\mu_F(T)=\mu_F(0)-\delta_\mu E_F(0)T^2$, $E_F(T)=E_F(0)[1-\delta E_F T^2]$. The systems Ge(1;1) and Si(2;1) are high-stress limits of normal germanium [Ge(4;2)] and silicon [Si(6;2)] when the stresses are along ⟨111⟩ and ⟨100⟩ directions, respectively. The results in GaP and SiC are calculated for two situations. Because of camel's back (CB) structure in GaP, there are six occupied conduction bands if the Fermi energy is less than the height of CB. On the other hand, if the Fermi energy exceeds the height of CB only three conduction bands are occupied. The two limiting configurations in SiC are (i) there are two occupied valence bands when spin-orbit coupling exceeds the whole Fermi energy, and (ii) there are three occupied valence bands when the spin-orbit coupling is negligible.

System	r_0	$-\epsilon_0$ (meV)	r_c	T_c (K)	δn (meV)$^{-2}$	$\delta\mu$ (meV)$^{-2}$	δE_F (meV)$^{-2}$	χ (meV^{-1}cm^3)
Ge(1;1)	1.62	2.95	2.80	3.75	6.32	1.62	4.75	2.09×10^{-16}
Ge(4;2)	0.57	6.07	0.97	8.71	1.15	0.25	0.85	4.53×10^{-18}
Si(2;1)	1.67	13.96	2.88	18.31	0.27	0.07	0.20	1.04×10^{-18}
Si(6;2)	0.84	22.49	1.44	30.29	0.10	0.02	0.07	0.86×10^{-19}
GaP(3;2)	1.00	25.14	1.72	33.19	0.08	0.02	0.06	0.72×10^{-19}
GaP(6;2)	0.90	27.16	1.54	32.72	0.08	0.02	0.06	0.48×10^{-19}
SiC(3;2)	0.98	40.14	1.68	56.05	0.03	0.007	0.02	0.16×10^{-19}
SiC(3;3)	0.76	42.58	1.30	59.14	0.03	0.006	0.02	0.98×10^{-20}

$$\frac{n_c}{n_0} \equiv \left[\frac{r_0}{r_c}\right]^3 = \frac{1}{20\epsilon'_{\mathrm{xc}}(r_0)}[2\epsilon'_{\mathrm{xc}}(r_c) - 2r_c\epsilon''_{\mathrm{xc}}(r_c) + r_c^2\epsilon'''_{\mathrm{xc}}(r_c)] \ . \tag{8}$$

Equation (7) has no explicit dependence on band parameters. Its solution is nearly a constant, $n_c/n_0 \simeq 0.20$. This is in agreement with Hansel's original observation[8] and the scaling relation derived by Reinecke and Ying.[10] Furthermore, in all the systems we have investigated using the general form for ϵ_{xc}, it is found that the ratio $\epsilon_0/k_B T_c \simeq 9$.[10]

In density-functional formalism the calculation of surface properties also requires a knowledge of exchange-correlation energy. A general expression like Eq. (5) for ϵ_{xc} easily allows the inclusion of exchange-correlation effects in local-density approximation.[11–13] Recently, Singwi and Tosi[14] used the ideas of Kohn and Yaniv[15] to propose a simple scaling relation for the surface energy, namely $\sigma\chi \sim a_{\mathrm{ex}}$ where χ is given by Eq. (7). From the coefficient of T^2 term in the low-temperature expansion of surface energy, Singwi and Tosi have obtained the critical temperature. It should be recognized that the general expression for ϵ_{xc} makes it easy to calculate many properties of EHL in a variety of semiconductors.

We have evaluated various properties of EHL in Ge(1;1), Ge(4;2), Si(6;2), GaP, and SiC using ϵ_{xc} from Eq. (5). The results given in Table I are in good agreement with experimental values.[16,17]

ACKNOWLEDGMENT

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