and the operator $|\alpha\rangle\langle\alpha|$ commutes with the Hamiltonian. The last expression is then

$$\frac{d}{dt}\langle\varphi_k(0)(\sum_\alpha|\alpha\rangle\langle\alpha|)\varphi_k(0)\rangle=0.$$

Thus we obtain

$$\sum_{k'}W_{kk'}=\sum_{k'}W_{k'k}=\left[\frac{d}{dt}|\langle\psi_k(t)|\varphi_k(t)\rangle|^2\right]_{t=0}.$$

This relation is also a consequence of the unitarity of the S-matrix.

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Correlation Energy in a Model Semiconductor

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The correlation energy of the electrons in a semiconductor is expected to be less than in a metal with the same electron density. The reduction occurs because the existence of an energy gap between filled and empty states tends to increase the magnitude of the energy denominators of perturbation theory. This effect is studied in a simple model, based on the calculations of Gell-Mann and Brueckner, in which the semiconductor is represented as a free electron gas with an energy gap above the Fermi surface. The correlation energy then depends on the ratio of the energy gap to the valence bandwidth as well as on the density. It is shown that for an energy gap large compared to the bandwidth, second order perturbation theory is correct; while for a small energy gap, an explicit correction to the Gell-Mann–Brueckner series can be obtained.

INTRODUCTION

THE correlation energy of electrons in semiconductors was first studied by Ufford[1] who applied second order perturbation theory to a simple model of a semiconductor. He showed that the second order theory gave a finite correlation energy (in opposition to the case of a metal in which a logarithmic divergence is found), but obtained a logarithmic dependence of the correlation energy on the energy gap. This conclusion requires revision in the light of the results of Gell-Mann and Brueckner[2] who showed, for a free electron gas, how the contributions from all orders of perturbation theory can be summed to give a finite correlation energy. The correlation energy in a semiconductor must approach this limit as the energy gap goes to zero.

It is impossible, in the present state of knowledge of wave functions in solids, to make a detailed calculation of the correlation energy of electrons in any real crystal. A simple model must be chosen. The essential feature in which a semiconductor or an insulator differs from a metal is in the presence of an energy gap in the one electron excitation spectrum. A simple model of a semiconductor would thus consist of a free electron gas (with an effective mass ratio m^*), which has an energy gap above the Fermi surface. All other effects of the crystal structure are to be ignored.

In the language of perturbation theory, we consider an infinite system with N electrons per unit volume which interact through Coulomb forces. The unperturbed wave functions of the system are Slater determinants of plane waves, but the energy of a one particle state of momentum p is

$$\begin{aligned}\epsilon(p)&=p^2/2mm^* && 0\le p\le p_F,\\ \epsilon(p)&=p^2/2mm^*+E_G && p>p_F,\end{aligned}\qquad(1)$$

where $p_F{}^3=3\pi^2\hbar^3N$. If the total energy of the lowest state of this system is calculated according to perturbation theory, with the Coulomb interaction as a perturbation, the Fermi energy and the exchange energy are the same as for the ordinary "free electron gas," but higher terms in the perturbation series are different because the energy gap, E_G, appears in the energy denominators.

The second order term in the perturbation series for the energy per particle can be written (following the work of Macke[3])

$$\begin{aligned}E_2=\frac{-3e^4}{16\hbar^2p_F{}^3\pi^5}\int d\mathbf{q}'\int_{\substack{p_1<p_F\\|\mathbf{p}_1+\mathbf{q}|>p_F}}d\mathbf{p}_1'\int_{\substack{p_2<p_F\\|\mathbf{p}_2+\mathbf{q}|>p_F}}d\mathbf{p}_2'\\ \times[\mathbf{q}'\cdot(\mathbf{p}_1'+\mathbf{p}_2'+\mathbf{q}')/mm^*+E_G]^{-1}\\ \times\left[\frac{1}{q'^4}-\frac{1}{2q'^2(\mathbf{p}_1'+\mathbf{p}_2'+\mathbf{q}')^2}\right].\end{aligned}\qquad(2)$$

It is convenient to introduce dimensionless vectors

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[1] C. W. Ufford, Phys. Rev. **59**, 598 (1941). The "exchange correlation energy" was neglected in this calculation.

[2] M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).

[3] W. Macke, Z. Naturforsch. **5a**, 192 (1950).

$\mathbf{q}$, $\mathbf{p}_1$, $\mathbf{p}_2$ such that $\mathbf{q}'=\mathbf{q}p_F$, $\mathbf{p}_1'=\mathbf{p}_1p_F$, $\mathbf{p}_2'=\mathbf{p}_2p_F$, and to introduce atomic units (with energy measured in rydbergs).

$$E_2=\frac{-3m^*}{8\pi^5}\int d\mathbf{q}\int_{\substack{p_1<1\\|\mathbf{p}_1+\mathbf{q}|>1}}d\mathbf{p}_1\int_{\substack{p_2<1\\|\mathbf{p}_2+\mathbf{q}|>1}}d\mathbf{p}_2 \times[\mathbf{q}\cdot(\mathbf{p}_1+\mathbf{p}_2+\mathbf{q})+\epsilon_G]^{-1} \times\left[\frac{1}{q^4}-\frac{1}{2q^2(\mathbf{p}_1+\mathbf{p}_2+\mathbf{q})^2}\right]. \quad (3)$$

In this equation $\epsilon_G=mm^*E_G/p_F^2=E_G/2E_F$ where E_F is the Fermi energy. It will be convenient in the following discussion to consider ϵ_G (rather than E_G) to be a given parameter, which characterizes a particular semiconductor. Higher terms in the perturbation series may be constructed in the manner of Gell-Mann and Brueckner. It is important to note that each energy denominator contains ϵ_G.

LIMIT OF LARGE ENERGY GAP

The character of the perturbation series is quite different according as the energy gap parameter ϵ_G is large or small compared to unity. The case of large energy gap is the simplest, and will be considered first. In that case, we may expand each term in the perturbation series in inverse powers of ϵ_G. The leading contribution from the second order is of order ϵ_G^{-1}, third order ϵ_G^{-2}, nth order ϵ_G^{-n+1}. Actually higher terms of the perturbation expansion are divergent, but we can easily sum the divergent parts of the series prior to integrating, in a manner exactly analogous to the Gell-Mann-Brueckner theory, and so obtain a finite correlation energy. The result contains terms of the order $\epsilon_G^{-2}\ln\epsilon_G$ coming from the elimination of divergences; but the second order determines the ϵ_G^{-1} term correctly.

To evaluate the coefficient of ϵ_G^{-1}, we can neglect the term $\mathbf{q}\cdot(\mathbf{q}+\mathbf{p}_1+\mathbf{p}_2)$ in the denominator compared to ϵ_G. We then have

$$E_2=\frac{-3m^*}{8\pi^5\epsilon_G}\left[\int\frac{d\mathbf{q}}{q^4}\int d\mathbf{p}_1\int d\mathbf{p}_2 -\frac{1}{2}\int\frac{d\mathbf{q}}{q^2}\int d\mathbf{p}_1\int d\mathbf{p}_2(\mathbf{q}+\mathbf{p}_1+\mathbf{p}_2)^{-2}\right], \quad (4)$$

(subject to the usual restriction on p_1 and p_2). The first integral can be done easily in a coordinate system suggested by Macke.[3] We obtain a contribution

$$-56m^*/15\pi^2\epsilon_G.$$

The second term is more complicated. For $q>2$, all values of p_1 and p_2 such that $p_1, p_2<1$ are allowed; for $q<2$ the limitations on the initial states render the volume element quite complicated. For $q>2$, we obtain a contribution $31/45\pi^2\epsilon_G$ while for $q<2$ a Monte Carlo integration gave $[0.45\pm0.03]/\pi^2\epsilon_G$. The result is then

$$E_2=-0.263m^*/\epsilon_G. \quad (5)$$

Since ϵ_G is itself proportional to m^*, the dependence on the effective mass in (5) is illusory, and we have

$$E_2=-0.263/\epsilon_G', \quad (5a)$$

where $\epsilon_G'=mE_G/p_F^2$, the ratio of the energy gap to twice the free electron bandwidth.

The complete second order perturbation integral (3) could, of course, be evaluated exactly, although the calculation would be quite lengthy. However all terms in the result of higher order than the first in ϵ_G^{-1} would be modified by higher order perturbations. Equations (5) and (5a) are, however, exact for this model in the limit of very large energy gap.

The result presented in Eq. (5) cannot be considered, however, to approximate the actual correlation energy of electrons in any real insulator. The limit of energy gap large compared to bandwidth occurs in materials for which the electrons are strongly localized on atoms; the case of extreme tight binding. Under these circumstances, the correlation energy, which is essentially the error in the energy computed in the Hartree-Fock approximation, is principally due to the failure of that approximation to yield the correct localization of electrons on individual atoms, and does not vanish in the limit of very large ϵ_G.

LIMIT OF SMALL ENERGY GAP

If the second order perturbation (3) is evaluated in the limit of small ϵ_G, a term proportional to $\ln\epsilon_G$ is obtained, as was first shown by Ufford.[1] However, if the perturbation series is summed prior to carrying out the integration over q, the result is not only finite at $\epsilon_G=0$, but possesses a finite first derivative (with respect to ϵ_G) as well. If the correlation energy in this model is expressed as a series in ϵ_G for small ϵ_G the zero order term must be the correlation energy of the ordinary free electron gas, which is given correctly by the Gell-Mann-Brueckner theory for small r_S. Then there is a term, proportional to ϵ_G, whose coefficient is a complicated function of r_S. If this coefficient is expanded in powers of r_S, we may expect the Gell-Mann-Brueckner treatment to give correctly the lowest two terms in this expansion, corresponding to the fact that two terms are also obtained for the free electron gas. The perturbation series does not possess a finite second derivative with respect to ϵ_G at $\epsilon_G=0$, so we must expect terms of the order $\epsilon_G^2\ln\epsilon_G$ to be present as well. Coefficients of such terms would also be given correctly by this treatment for high density, but to evaluate the correlation energy for arbitrary ϵ_G, though possible in principle, would require very extensive numerical integration. We will obtain here only the coefficient of ϵ_G.

Following Gell-Mann and Brueckner, the correlation energy per particle at high density is given by

$$E_C=\frac{-12m^*}{\pi^3}\int_{-\infty}^{\infty}du\int_0^2\frac{dq}{q}\times\left[\frac{q^2R(q,u)}{\lambda}-\left(\frac{q^2}{\lambda}\right)^2\ln\left(1+\frac{\lambda R}{q^2}\right)\right]+\delta+\epsilon_b^{(2)}, \quad (6)$$

where $\lambda=4m^*/\pi p_F=4m^*\alpha r_S/\pi$; δ is a term added to ensure that all second order contributions are included, and $\epsilon_b^{(2)}$ is the exchange correlation energy. The dependence on the energy gap is incorporated in the function $R(q,u)$. This equation is obtained by carrying out the summation involved in Eq. (22) of reference (2).

The presence of an energy gap modifies the propagator employed by Gell-Mann and Brueckner to reproduce the energy denominators of perturbation theory. With reference to Eq. (12) of reference (2) we use as propagator

$$F_q(t)=\int_{\substack{p<1\\|\mathbf{p}+\mathbf{q}|>1}}d\mathbf{p}\exp[-|t|(\tfrac{1}{2}q^2+\mathbf{q}\cdot\mathbf{p}+\tfrac{1}{2}\epsilon_G)]. \quad (7)$$

The function $R(q,u)$ is then

$$R(q,u)=\frac{1}{4\pi}\int_{\substack{p<1\\|\mathbf{p}+\mathbf{q}|>1}}d\mathbf{p}\int_{-\infty}^{\infty}e^{ituq}\times\exp[-|t|(\tfrac{1}{2}q^2+\mathbf{q}\cdot\mathbf{p}+\tfrac{1}{2}\epsilon_G)]dt. \quad (8)$$

The integration required to obtain an exact evaluation of (8) would be very complicated, and the result would not be very useful since only a fraction of the entire perturbation series is included. However, to obtain results valid at high density, it suffices to make sure the apparent divergence in second order (for the ordinary free electron gas) is properly removed, and this can be accomplished by using a small q approximation in (8). Then

$$R(q,u)=\frac{q}{2}\int_0^1 xdx\int_{-\infty}^{\infty}e^{ituq}\exp[-|t|(qx+\epsilon_G/2)]dt. \quad (9)$$

Although this integral is relatively simple to evaluate, the result is still complicated, and the remaining integrations involved in Eq. (6) become quite difficult. We proceed to expand E_C as given by (6) for small ϵ_G

$$E_C(\epsilon_G)=E_C(0)+\epsilon_G\left(\frac{\partial E_C}{\partial\epsilon_G}\right)_0+O(\epsilon_G^2,\epsilon_G^2\ln\epsilon_G). \quad (10)$$

The leading term $E_C(0)$ is the Gell-Mann-Brueckner formula[4] (with an effective mass m^*). We differentiate Eq. (6) with respect to ϵ_G and find[5]

$$\left(\frac{\partial E_C}{\partial\epsilon_G}\right)_0=-\frac{12m^*}{\pi^3}\int_{-\infty}^{\infty}du\int_0^2\frac{dq}{q}R_0(u)\times\left(\frac{\partial R}{\partial\epsilon_G}\right)_0\frac{1}{1+\lambda R_0/q^2}+\left(\frac{\partial\delta}{\partial\epsilon_G}\right)_0+\left(\frac{\partial\epsilon_b^{(2)}}{\partial\epsilon_G}\right)_0. \quad (11)$$

We will consider $\partial\delta/\partial\epsilon_G$ and $\partial\epsilon_b^{(2)}/\partial\epsilon_G$ separately. We must now determine $R(q,u)$. From (9)

$$R(q,u)=q\int_0^1\frac{(qx+\epsilon_G/2)}{(qx+\epsilon_G/2)^2+q^2u^2}xdx. \quad (12)$$

Thus

$$\left(\frac{\partial R}{\partial\epsilon_G}\right)_0=\frac{1}{2q}\int_0^1\frac{(u^2-x^2)}{(u^2+x^2)^2}xdx=-\frac{1}{4q}[\ln(1+1/u^2)-2/(u^2+1)]. \quad (13)$$

We find also, in agreement with reference (2)

$$[R(q,u)]_{\epsilon_G=0}\equiv R_0(u)=1-u\tan^{-1}(1/u). \quad (14)$$

The integration over q in Eq. (11) can now be performed. Put $S(u)=-q(\partial R/\partial\epsilon_G)$. We then have after making a high-density expansion

$$\int_{-\infty}^{\infty}duR_0(u)S(u)\int_0^2[q^2(1+\lambda R_0(u)/q^2)]^{-1}dq=\frac{1}{2}\int_{-\infty}^{\infty}S(u)\left[\pi\left(\frac{R_0}{\lambda}\right)^{\frac{1}{2}}-R_0\right]du.$$

The remaining integrals have been evaluated numerically. The result is

$$\left(\frac{\partial E_C}{\partial\epsilon_G}\right)_0=0.144(m^*p_F)^{\frac{1}{2}}-0.0587m^*+O(r_s)+\left(\frac{\partial\delta}{\partial\epsilon_G}\right)_0+\left(\frac{\partial\epsilon_b^{(2)}}{\partial\epsilon_G}\right)_0. \quad (15)$$

It is now necessary to evaluate the last two terms in (15). In a manner analogous to reference (2), we have

$$\delta=-\frac{3m^*}{8\pi^5}\int\frac{d\mathbf{q}}{q^4}\int_{\substack{p_1<1\\|\mathbf{p}_1+\mathbf{q}|>1}}d\mathbf{p}_1\int_{\substack{p_2<1\\|\mathbf{p}_2+\mathbf{q}|>1}}d\mathbf{p}_2\times[\mathbf{q}\cdot(\mathbf{p}_1+\mathbf{p}_2+\mathbf{q})+\epsilon_G]^{-1}+\frac{6m^*}{\pi^2}\int_0^2dq\int_0^1xdx\int_0^1ydy\times[q(x+y)+\epsilon_G]^{-1}. \quad (16)$$

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[4] $E_C(0)=m^*[0.062\ln m^*r_s-0.096]$.

[5] The limits of integration in (11) are slightly modified from those of reference (2). A corresponding change has been made in δ.

Then

$$\left(\frac{\partial\delta}{\partial\epsilon_G}\right)_0=+\frac{3m^*}{8\pi^5}\int\frac{d\mathbf{q}}{q^4}\int_{\substack{p_1<1\\|\mathbf{p}_1+\mathbf{q}|>1}}d\mathbf{p}_1\int_{\substack{p_2<1\\|\mathbf{p}_2+\mathbf{q}|>1}}d\mathbf{p}_2$$
$$\times[q\cdot(\mathbf{p}_1+\mathbf{p}_2+\mathbf{q})]^{-2}-\frac{6m^*}{\pi^2}\int_0^2\frac{dq}{q^2}\int_0^1 xdx\int_0^1 ydy$$
$$\times(x+y)^{-2}. \quad (17)$$

The first integral can be done in a fashion suggested by Macke.[3] The quantity $(\partial\delta/\partial\epsilon_G)_0$ is actually finite since the apparently divergent terms cancel if the integrands are combined, prior to integrating over q. The result is

$$\left(\frac{\partial\delta}{\partial\epsilon_G}\right)_0=-0.0429m^*.$$

There remains the second order exchange correlation term. From Eq. (3) we find

$$\left(\frac{\partial\epsilon_b^{(2)}}{\partial\epsilon_G}\right)_0=-\frac{3m^*}{16\pi^5}\int\frac{d\mathbf{q}}{q^2}\int_{\substack{p_1<1\\|\mathbf{p}_1+\mathbf{q}|>1}}d\mathbf{p}_1\int_{\substack{p_2<1\\|\mathbf{p}_2+\mathbf{q}|>1}}d\mathbf{p}_2$$
$$\times\{(\mathbf{q}+\mathbf{p}_1+\mathbf{p}_2)^2[\mathbf{q}\cdot(\mathbf{q}+\mathbf{p}_1+\mathbf{p}_2)]\}^{-1}. \quad (18)$$

This integral is quite complicated. It has been approximated in the following manner. For $q<2$, we set $(\mathbf{q}+\mathbf{p}_1+\mathbf{p}_2)^2=q^2+1$, following a suggestion of Hubbard.[6] For $q>2$, we set $(\mathbf{q}+\mathbf{p}_1+\mathbf{p}_2)^2=q^2$. Under these approximations

$$\left(\frac{\partial\epsilon_b^{(2)}}{\partial\epsilon_G}\right)_0=-0.056m^*.$$

Then the final result is

$$\begin{aligned}E_C(\epsilon_G)-E_C(0)&=[0.144(m^*p_F)^{\frac{1}{2}}-0.158m^*]\epsilon_G\\&=[0.200(m^*/r_S)^{\frac{1}{2}}-0.158m^*]\epsilon_G.\end{aligned} \quad (19)$$

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