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Electron Correlation

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The state of a real gas of electrons of uniform density is examined. An equation for the coordinate representation of the density matrix for two particles is found which satisfies the various necessary conditions and which gives a lower energy than the antisymmetrized Single Slater Determinant. The additional negative correlation energy found is proportional to the one-sixth power of the density at high densities.

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1. INTRODUCTION

WE wish to discuss the electron correlation energy in a system of electrons of uniform density and infinite extent. Start with a finite system of N electrons in a volume, V, and of density:

$$\rho_0=N/V. \tag{1.1}$$

In order that the density of electrons be kept constant, assume that there is a uniform density of positive charge, $e\rho_0$. If the unit of length is chosen to be one Bohr radius,

$$a_0=h^2/4\pi^2me^2, \tag{1.2}$$

and the unit of energy is the atomic unit,

$$e^2/a_0=27.21 \text{ ev}, \tag{1.3}$$

then the Hamiltonian of the system is

$$H=\tfrac{1}{2}\sum_{i=1}^{i=N}-\nabla_i\cdot\nabla_i+\sum_{N\geq i>j\geq 1}\sum(1/r_{ij}) -a_0{}^3\rho_0\sum_{i=1}^{i=N}\iiint_V(1/r_{i0})d\mathbf{r}_0 +\tfrac{1}{2}a_0{}^6\rho_0{}^2\int\cdots\int_V(1/r_{01})d\mathbf{r}_1d\mathbf{r}_0. \tag{1.4}$$

The last constant term is the self-energy of the continuous positive charge which is added to the Hamiltonian for convenience. This term depends upon the shape of the system, and diverges at infinite volume, but cancels with the major terms in the potential of the electrons.

It is convenient to change to the equally dimensionless coordinates, x, which are $\rho_0{}^{\frac{1}{3}}$ times the metric length,

$$\mathbf{x}=a_0\rho_0{}^{\frac{1}{3}}\mathbf{r}=c^{\frac{1}{3}}\mathbf{r}, \tag{1.5}$$

where $\mathbf{r}$ is the dimensionless coordinate used in Eq. (1.4), and

$$c=\rho_0a_0{}^3, \tag{1.6}$$

so that c is the concentration of electrons per cubic Bohr radius. In these units the Hamiltonian is

$$H=\tfrac{1}{2}c^{\frac{2}{3}}\sum_{i=1}^{i=N}-\nabla_i\cdot\nabla_i+c^{\frac{1}{3}}\left\{\sum_{N\geq i>j\geq 1}\sum(1/x_{ij}) -\sum_{i=1}^{i=N}\iiint_N(1/x_{i0})d\mathbf{x}_0 +\frac{1}{2}\int\cdots\int_N(1/x_{01})d\mathbf{x}_0d\mathbf{x}_1\right\}. \tag{1.7}$$

The usual zeroth-order solution is to assume a Single Slater Determinant of plane waves with a minimum kinetic energy. With this zeroth-order solution, the kinetic energy per electron is known to be,

$$\epsilon_{0k}=(9\pi/10)(\pi/3)^{\frac{1}{3}}c^{\frac{2}{3}}, \tag{1.8}$$

and the total potential energy per electron to be,

$$\epsilon_{0p}=-(3/4)(3/\pi)^{\frac{1}{3}}c^{\frac{1}{3}}. \tag{1.9}$$

The major terms in potential energy have been made to cancel to zero by the inclusion of the self-energy of the uniform positive charge. The term, ϵ_{0p}, of Eq. (1.9) is due to the fact that the Single Slater Determinant implies a certain correlation in the position of electrons with equal spin, namely that no two electrons of the same spin approach each other infinitely closely. The term ϵ_{0p} is usually called the exchange energy. We shall attempt in this paper to derive an expression describing a state of the system which is no longer a Single Slater Determinant, and which gives a lower energy, namely one in which the energy is

$$\epsilon=\epsilon_{0k}+\epsilon_{0p}+\Delta\epsilon_c, \tag{1.10}$$

where $\Delta\epsilon_c$ will be called the correlation energy and will be given in units of double Rydbergs, e^2/a_0, Eq. (1.3).

The electron correlation energy, $\Delta\epsilon_c$, is made up of two terms, one of them positive, namely an increase in the kinetic energy, and the second term negative, due to an increased correlation between the electrons such that they are on the average less close together than given by the Single Slater Determinant solution. The units of length, $\rho_0{}^{-\frac{1}{3}}$, which we are using are now such that the density is unity. Let us define conceptually a function, $F_2(\mathbf{x}_1,\mathbf{x}_2)$, by the statement that F_2 shall represent the probability density that one will simultaneously have an electron at the position $\mathbf{x}_1$ and another electron at the position $\mathbf{x}_2$. For large distances, x_{12}, between the electrons, F_2 should approach unity in value. We therefore write

$$F_2(\mathbf{x}_1,\mathbf{x}_2)=1-g(x_{12}). \tag{1.11}$$

Since the integral of F_2 over $d\mathbf{x}_1 d\mathbf{x}_2$ over the volume of the system, which in these units is N, must be equal to $N(N-1)$, we have that

$$\int_0^\infty 4\pi x^2 g(x)dx=1. \tag{1.12}$$

Due to the cancellation of the major terms, the potential energy of the system is

$$\epsilon_p=-\tfrac{1}{2}c^{\frac{1}{3}}\int_0^\infty 4\pi x g(x)dx. \tag{1.13}$$

The value of ϵ_{0p} given by Eq. (1.9), is obtained by putting into Eq. (1.13) the value

$$g_0(x)=\tfrac{1}{2}f_0^2(x), \tag{1.14}$$

where f_0 is the expression for the single particle density matrix element in coordinate representation appropriate to a Single Slater Determinant of plane waves of minimum energy, namely

$$\begin{aligned} f_0(x)&=3\left\{\frac{\sin[(3\pi^2)^{\frac{1}{3}}x]}{[(3\pi^2)^{\frac{1}{3}}x]^3}-\frac{\cos[(3\pi^2)^{\frac{1}{3}}x]}{[(3\pi^2)^{\frac{1}{3}}x]^2}\right\} \\ &\cong 1-(1/10)(3\pi^2)^{\frac{2}{3}}x^2+\cdots. \end{aligned} \tag{1.15}$$

The kinetic energy is also determined by f and is

$$\epsilon_k=\tfrac{3}{2}c^{\frac{2}{3}}[-(\partial^2/\partial x^2)f(x)]_{x=0}, \tag{1.16}$$

which leads to the numerical value of Eq. (1.8) with Eq. (1.15) for f. The derivation of these relationships is given in Sec. 2 of this paper.

The method which we propose to use is as follows: we introduce the coordinate representation, $\rho_2(\mathbf{x}_1',\mathbf{x}_1'';\mathbf{x}_2',\mathbf{x}_2'')$, of the density matrix of two particles.[1] The diagonal element, namely that obtained when $\mathbf{x}_i'=\mathbf{x}_i''=\mathbf{x}_i$ in ρ_2, is the function F_2 of Eq. (1.11), and hence by that equation determines g and the total potential energy by Eq. (1.13). If $\mathbf{x}_2'=\mathbf{x}_2''=\mathbf{x}_2$, is set in F_2 and the function is integrated over $d\mathbf{x}_2$, one obtains a function $f(x)$, where $x=|\mathbf{x}_1'-\mathbf{x}_1''|$. This function, $f(x)$ is the coordinate representation of the density matrix for single particles, and determines the kinetic energy by Eq. (1.16).

Now there are a number of necessary conditions which must be satisfied by ρ_2. Some of these are symmetry conditions and others are conditions which must be satisfied by the function $f(x)$. The most significant of the latter is imposed by the demand that the original eigenfunction, ψ, be antisymmetric in all particle exchanges. This requires that if $f(x)$ is regarded as a function of two coordinates and brought into diagonal form, the coefficients of any of the diagonal terms must lie between zero and two, expressing the condition that only two electrons with opposite spin can occupy one single-particle quantum state. In this case of uniform density, the diagonal form of $f(x)$ is given by a transformation to plane waves, and the condition simplifies to the statement that the Fourier transform of $f(x)$ in three dimensions is limited to lie between 0 and 2 in value.

We then set up a simple form for ρ_2 which satisfies the necessary conditions and try to determine, subject to this simple form, the function which minimizes the total energy. Actually, even subject to the simple form assumed, only an approximation to the best analytical function to minimize the energy is found.

One may easily see what the minimum possible potential energy is. The minimum value of ϵ_p given by Eq. (1.13) in view of (1.12) is satisfied if

$$\begin{aligned} g_m(x)&=1, \quad 0\le x\le (3/4\pi)^{\frac{1}{3}}, \\ g_m(x)&=0, \quad (3/4\pi)^{\frac{1}{3}}<x\le\infty, \end{aligned} \tag{1.17}$$

namely, when no two electrons can get within a distance $(3/4\pi)^{\frac{1}{3}}$ of each other. With this $g(x)$ in Eq. (1.13) for the potential energy, one finds

$$\begin{aligned} \epsilon p_{\min}&=-(3/2)(\pi/6)^{\frac{1}{3}}c^{\frac{1}{3}} \\ &=(2\pi/3)^{\frac{2}{3}}\epsilon_{0p}=1.637\,\epsilon_{0p}. \end{aligned} \tag{1.18}$$

The correct expressions for $\Delta\epsilon_c$, Eq. (1.10), must lie between zero and this value. The Single Slater Determinant solution gives $g(x)=\frac{1}{2}$ at $x=0$ since there is correlation only between electrons of the same spin. It is interesting to look at the numbers obtained if one sets $g_0(x)=\frac{1}{2}$ for x between 0 and $(3/2\pi)^{\frac{1}{3}}$. This would be the optimum form if there were correlation only between electrons of equal spin. One then satisfies Eq. (1.12) and finds

$$\begin{aligned} &\epsilon p_{\min}(\text{correlation same spin only}) \\ &\qquad =2^{-\frac{1}{3}}\epsilon p_{\min}=1.299\,\epsilon_{0p}. \end{aligned} \tag{1.18'}$$

2. DENSITY MATRIX ELEMENTS

In this section we propose to define the density matrix element for paired particles, to discuss its properties, and incidentally to derive some of the equations introduced in the last section. The three dimensional space coordinates that we use are $\mathbf{x}_i=\rho_0^{\frac{1}{3}}$ times the metric coordinate of electron i, so that the volume of the system containing N particles is N. The symbol $q_i=\mathbf{x}_i,\sigma_i$ is used for the three-dimensional space coordinate and the spin coordinate, σ_i. The state of the system is given by the normalized eigenfunction $\psi(q_1,q_2,\cdots,q_n)$. The Hamiltonian of the system is given

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[1] Since preparation of this manuscript a paper has appeared by Per O. Löwdin, Phys. Rev. **97**, 1474 (1955), describing the properties of this and similarly defined density matrices.

by the Eq. (1.7), in which the self-energy of the uniform positive charge has been included. Now define the element of the density matrix including spin for two particles by the equation,

$$\rho_{2\sigma}(q_1',q_1'';q_2',q_2'')=N(N-1)\int\int\cdots\int\psi^*(q_1',q_2',q_3,\cdots,q_N)\times\psi(q_1'',q_2'',q_3,\cdots,q_N)dq_3\cdots dq_N, \quad (2.1)$$

and the element of the coordinates of position alone by

$$\rho_2(\mathbf{x}_1',\mathbf{x}_1'';\mathbf{x}_2',\mathbf{x}_2'')=\int\int\rho_{2\sigma}(\mathbf{x}_1',\sigma_1,\mathbf{x}_1'',\sigma_1;\mathbf{x}_2',\sigma_2,\mathbf{x}_2'',\sigma_2)d\sigma_1 d\sigma_2, \quad (2.2)$$

in which the integration is carried over the diagonal elements of both spins. The density matrix element ρ_1 in the coordinates of a single particle is defined by

$$\rho_1(\mathbf{x}_1',\mathbf{x}_2'')=[1/(N-1)]\int\int\int\rho_2(\mathbf{x}_1',\mathbf{x}_1'';\mathbf{x}_2,\mathbf{x}_2)d\mathbf{x}_2. \quad (2.3)$$

The energy of the system is given by

$$E=\int\psi^*H\psi dq_1\cdots dq_N, \quad (2.4)$$

and the result is seen to be expressible as

$$E=-\tfrac{1}{2}c^{\frac{2}{3}}\int\int\int[\nabla''\cdot\nabla''\rho_1(\mathbf{x}',\mathbf{x}'')]_{\mathbf{x}'=\mathbf{x}''=\mathbf{x}}\,d\mathbf{x}+\tfrac{1}{2}c^{\frac{1}{3}}\int\int\cdots\int[\rho_2(\mathbf{x}_1,\mathbf{x}_1;\mathbf{x}_2,\mathbf{x}_2)-1]d\mathbf{x}_1 d\mathbf{x}_2, \quad (2.5)$$

where the operator ∇'' operates only on x'' in ρ_1. The diagonal elements of ρ_2 are equal to the probability density function F_2 defined conceptually in the last section, and we write

$$\rho_2(\mathbf{x}_1,\mathbf{x}_1;\mathbf{x}_2,\mathbf{x}_2)=F_2(\mathbf{x}_1,\mathbf{x}_2)=1-g(x_{12}),\quad x_{12}=|\mathbf{x}_1-\mathbf{x}_2|, \quad (2.6)$$

in which the fact that the number density is independent of position and equal to unity has been used. The density matrix for single particles is written as

$$\rho_1(\mathbf{x}',\mathbf{x}'')=f(x),\quad x=|\mathbf{x}'-\mathbf{x}''|,\quad f(0)=1. \quad (2.7)$$

Since both expressions in (2.5) are independent of the diagonal coordinate, one may divide by the total number of particles to obtain the energy per particle by omitting one integration. The operation $(\nabla''\cdot\nabla'')_{x'=x''}=[(2/x)d/dx+d^2/dx^2]_{x=0}=3[d^2/dx^2]_{x=0}$, since f is regular and even at $x=0$. One has

$$E/N=\epsilon=\tfrac{3}{2}c^{\frac{2}{3}}[-(d^2/dx^2)f(x)]_{x=0}-\tfrac{1}{2}c^{\frac{1}{3}}\int_0^\infty 4\pi x g(x)dx. \quad (2.8)$$

The first term on the right is the kinetic energy of Eq. (1.16) and the second term is the potential energy of Eq. (1.13).

Even in the more general case the energy of the system is completely determined by the density matrix element, $\rho_{2\sigma}$ of Eq. (2.1) provided none of the terms in the Hamiltonian contain the coordinates of three particles explicitly. As long as the Hamiltonian does not depend upon spin, the energy is determined completely by the elements integrated over the spin given by Eq. (2.2). Instead of seeking the eigenfunction ψ which gives the lowest energy, one may seek the density matrix element which leads to the lowest energy of the system. However the function $\rho_{2\sigma}$ must obey certain symmetry conditions. If P' is an operator that commutes the two primed indices, P'' an operator that commutes the two double primed indices, and P^* an operator that commutes the primes with the double primes, then

$$P'\rho_{2\sigma}=-\rho_{2\sigma},\quad P''\rho_{2\sigma}=-\rho_{2\sigma},\quad P^*\rho_{2\sigma}=\rho_{2\sigma}^*. \quad (2.9)$$

Since the Hamiltonian is real, we can choose a real solution, and write the third condition as $P^*\rho_{2\sigma}=\rho_{2\sigma}$. In addition to this an integral relationship on the diagonal element must be satisfied, namely

$$\int\int\int\rho_2(\mathbf{x}_1,\mathbf{x}_1;\mathbf{x}_2,\mathbf{x}_2)d\mathbf{x}_2=(N-1)\rho_1(\mathbf{x}_1,\mathbf{x}_1)=N-1, \quad (2.10)$$

as well as the condition that the density matrix element for a single particle is given by the integral of Eq. (2.3). The application of Eq. (2.10) leads to the limitation of Eq. (1.12) on $g(x)$, namely that its integral over three dimensional space be unity.

The element ρ_1 for a single particle must be Hermitian, and therefore, if real, $f(x)$ must be even in x, and if brought into diagonal form, ρ_1 must contain elements which lie between 0 and 2 in value, since only two electrons of opposite spin can occupy one state. Since ρ_1 depends only on the distance between the coordinates, its diagonal form is obtained by the coefficients of plane waves, or is just the three dimensional Fourier transform of $f(x)$. This transform is the function:

$$\phi(t)=\int 4\pi x^2 f(x)\frac{\sin 2\pi xt}{2\pi xt}dx,\qquad f(x)=\int 4\pi t^2\phi(t)\frac{\sin 2\pi xt}{2\pi xt}dt, \quad (2.11)$$

where t has the physical significance,

$$t=|\mathbf{P}|/h\rho_0^{\frac{1}{3}}, \tag{2.12}$$

and $\mathbf{p}$=momentum. The condition,

$$0\leq\phi(t)\leq 2, \tag{2.13}$$

must be satisfied. The physical significance of $\phi(t)$ is that it represents the total square amplitude of the single particle plane-wave function of momentum $\mathbf{p}$ in the total eigenfunction of the system. The condition that $f(x)$ at $x=0$ should be unity imposes the limitation that

$$\int 4\pi t^2\phi(t)dt=1, \tag{2.14}$$

which can be readily seen by putting $x=0$ into the second part of Eq. (2.11). The conditions of Eqs. (2.9), (2.10), (2.13), and (2.14) with ϕ connected to ρ_2 by the sequence of Eqs. (2.2), (2.3), and (2.11), must be imposed on $\rho_{2\sigma}$.

We now propose to suggest a very simple form for ρ_2 which satisfies the symmetry conditions for Eq. (2.9). This form will not be that which gives the minimum energy of the system, which in turn would be the exact solution of the problem, but we will limit ourselves to solutions which follow the form suggested. With this form we shall then attempt to approximately minimize the total energy subject to the other conditions.

Any additive term in $\rho_{2\sigma}$ may be written as the product of the function of the coordinates times the function of spin. For two electrons one can write one antisymmetric spin function and three symmetric functions. We will write, therefore, for the spatial part

$$\rho_2=\tfrac{3}{4}\rho_{2A}+\tfrac{1}{4}\rho_{2S}, \tag{2.15}$$

where the function ρ_{2A} which is to be multiplied by the three symmetric spin functions must obey the same symmetry conditions as Eq. (2.9), whereas ρ_{2S}, which is multiplied by the antisymmetric spin function obeys the conditions Eq. (2.9) with plus signs for the first two operators. A function of the form

$$\begin{aligned}\rho_{2A,\,S}=[&f(|\mathbf{x}_1'-\mathbf{x}_1''|)f(|\mathbf{x}_2'-\mathbf{x}_2''|)\\ &\mp f(|\mathbf{x}_1'-\mathbf{x}_2''|)f(|\mathbf{x}_2'-\mathbf{x}_1''|)]\\ &\times[1-k(|\mathbf{x}_1'-\mathbf{x}_2'|)][1-k(|\mathbf{x}_1''-\mathbf{x}_2''|)],\end{aligned} \tag{2.16}$$

satisfies the symmetry condition for ρ_{2A} with the minus sign, and for ρ_{2S} with the plus sign. The correct function ρ_2 could always be written as a sum of functions of this form. We will assume that there is only one function of the antisymmetric kind with triple weight, and one of the symmetric with single weight, and that they occur with the same function f and the same function k, where both f and k are real even functions of their variables. If the expression obtained is inserted in Eq. (2.3) for ρ_1, one finds indeed that in the limit $N\rightarrow\infty$, the function f is equal to ρ_1, namely Eq. (2.7). We thus obtain for the diagonal element of the pair density matrix,

$$F_2(\mathbf{x}_1,\mathbf{x}_2)=[1-\tfrac{1}{2}f^2(x_{12})][1-k(x_{12})]^2, \tag{2.17}$$

and for g, from Eq. (2.6):

$$g(x)=\tfrac{1}{2}f^2(x)+[1-\tfrac{1}{2}f^2(x)][2k(x)-k^2(x)]. \tag{2.18}$$

We now wish to find k and f such that

$$\int 4\pi x^2 g(x)dx=1, \tag{2.19}$$

that ϕ defined by Eq. (2.11), satisfies the conditions (2.13) and (2.14), and that the total energy be a minimum.

The Single Slater Determinant solution of lowest energy has f equal to f_0 given by Eq. (1.15) for which the Fourier transform is $\phi_0(t)$,

$$\begin{aligned}\phi_0(t)&=2 \quad 0\leq t\leq(3/8\pi)^{\frac{1}{3}},\\ \phi_0(t)&=0 \quad (3/8\pi)^{\frac{1}{3}}<t\leq\infty.\end{aligned} \tag{2.20}$$

This solution satisfies Eq. (2.14) as well as the condition of Eq. (2.13). It corresponds to full use of every plane wave of minimum energy up to $t=(3/8\pi)^{\frac{1}{3}}$, or from Eq. (2.12), the momentum, p, having all values less than $p_{\max}=\rho_0^{\frac{1}{3}}h(3/8\pi)^{\frac{1}{3}}$. With this solution for f the condition (2.19) demands that k be zero everywhere since the integral over the three dimensional space of $\frac{1}{2}f_0^2(x)$ is unity.

3. ANALYTICAL FORM OF THE FUNCTIONS

The next step is to find the analytical form of k and f that minimizes the total energy, subject to the conditions to be imposed on these functions. We first determine the form of k for fixed f, and secondly find a form for f that minimizes an approximation to the energy. We thus obtain a simple, but approximate, form for $f(x)$ containing one parameter to be adjusted so as to minimize the energy.

Since $k(x)$ does not directly enter into the expression (1.16) for the kinetic energy the best form for k, with $f(x)$ fixed, is that which minimizes the potential energy, Eq. (1.13), subject to the condition (1.12) that the integral of $g(x)$ over three dimensional space be unity. This is best satisfied by having $F_2=1-g$ as small as possible near the origin, or from (2.17) having $k\equiv 1$ for $0\leq x\leq x_0$, and zero for greater x. The value of x_0 up to which k be unity is to be determined from the condition (1.12) on the integral of g.

Define k by

$$\begin{aligned}k(x)&=1 \quad 0\leq x\leq x_0,\\ &=0 \quad x_0<x\leq\infty,\end{aligned} \tag{3.1}$$

and since $k^2=k$ everywhere, from (2.18)

$$g(x)=\tfrac{1}{2}f^2(x)+[1-\tfrac{1}{2}f^2(x)]k(x), \tag{3.2}$$

$$\begin{aligned}g(x)&=1 & 0\leq x\leq x_0,\\ &=\tfrac{1}{2}f^2(x) & x_0<x\leq\infty.\end{aligned} \tag{3.2'}$$

Now define four integrals of f,

$$\begin{aligned} I_2&=1-\frac{1}{2}\int 4\pi x^2 f^2(x)dx,\\ I_1&=\tfrac{3}{2}(3/\pi)^{\frac{1}{3}}-\frac{1}{2}\int 4\pi x f^2(x)dx,\\ J_2(x_0)&=\tfrac{2}{3}\pi x_0^3-\frac{1}{2}\int_0^{x_0} 4\pi x^2 f^2(x)dx,\\ J_1(x_0)&=\pi x_0^2-\frac{1}{2}\int_0^{x_0} 4\pi x f^2(x)dx. \end{aligned} \tag{3.3}$$

The limit x_0 beyond which $k(x)$ is zero is determined by (1.12) as

$$\begin{aligned} (2\pi/3)x_0^3+1-I_2+J_2(x_0)&=1,\\ x_0&=(3/2\pi)^{\frac{1}{3}}[I_2-J_2(x_0)]^{\frac{1}{3}}. \end{aligned} \tag{3.4}$$

Since $f(x=0)$ is unity, f is even, and hence $f'(x=0)=0$; we may then assume that for small x_0 the function J_2 is negligible. Hence, approximately,

$$x_0\cong(3/2\pi)^{\frac{1}{3}}I_2^{\frac{1}{3}}. \tag{3.4$'$}$$

The potential energy, ϵ_p, is given by (1.13) as

$$\begin{aligned} \epsilon_p&=-\tfrac{1}{2}c^{\frac{1}{3}}\int 4\pi x g(x)dx\\ &=-\tfrac{1}{2}c^{\frac{1}{3}}[\tfrac{3}{2}(3/\pi)^{\frac{1}{3}}+\pi x_0^2-I_1+J_1(x_0)]. \end{aligned} \tag{3.5}$$

Use the value of ϵ_{0p} given by (1.9) to write this as

$$\epsilon_p=\epsilon_{0p}-\tfrac{1}{2}c^{\frac{1}{3}}[\pi x_0^2-[I_1-J(x_0)]]. \tag{3.6}$$

In this expression assume I_1-J_1 to be negligible, and use the approximation of (3.4′) for x_0. One finds

$$\epsilon_p\cong\epsilon_{0p}-(3/4)(2\pi/3)^{\frac{1}{3}}c^{\frac{1}{3}}I_2^{\frac{2}{3}}. \tag{3.6$'$}$$

We use this approximation to determine the analytical form of $f(x)$.

Actually it is easier to discuss the form of the three-dimensional Fourier transform, $\phi(t)$, related to f by (2.11). The Fourier transform has the property that

$$\int 4\pi t^2\phi^2(t)dt=\int 4\pi x^2 f^2(x)dx=2(1-I_2). \tag{3.7}$$

The kinetic energy is given in terms of $\phi(t)$ by the relation,

$$\epsilon_k=2\pi^2c^{\frac{2}{3}}\int 4\pi t^4\phi(t)dt, \tag{3.8}$$

and of course ϕ must be restricted to obey the condition (2.14) on its integral over three-dimensional space.

Now find ϕ that minimizes

$$\epsilon_k+\epsilon_p-\lambda\int 4\pi t^2\phi(t)dt,$$

with λ an undetermined multiplier of the condition (2.14). Using the approximate form (3.6′) for ϵ_p and (3.7) to determine I_2 by an integral over ϕ^2, one finds

$$\phi=a-bt^2,$$

with a and b rather complicated constants, independent of t. However, condition (2.13) limits ϕ to lie between zero and two. Hence we set $\phi(t)=2$ for $0\leq t\leq t_1$, $\phi(t)=2-b(1-t^2/t_1^2)$ from $t_1\leq t\leq t_1(2b^{-1}-1)^{\frac{1}{2}}$, and $\phi(t)=0$ for greater values of t. We leave b arbitrary, but use the condition (2.14) on the integral to eliminate one of the parameters, t_1 or t_2. Finally it is simpler to convert to a new variable,

$$\tau=\tau_0^{-1}(8\pi/3)^{\frac{1}{3}}t=\tau_0^{-1}(8\pi/3)^{\frac{1}{3}}|\mathbf{p}|/h\rho_0^{\frac{1}{3}}, \tag{3.9}$$

where τ_0 is related to the single parameter, γ, by the equation,

$$\begin{aligned} \tau_0&=\{[1/10\gamma][(1+\gamma)^5-(1-\gamma)^5]\}^{-\frac{1}{3}}\\ &=[1+2\gamma^2+\tfrac{1}{5}\gamma^4]^{-\frac{1}{3}}, \end{aligned} \tag{3.10}$$

and write,

$$\begin{aligned} \phi(t)=\Phi(\tau)&=2 && 0\leq\tau\leq 1-\gamma,\\ &=2[1/4\gamma][(1+\gamma)^2-\tau^2] && 1-\gamma\leq\tau\leq 1+\gamma,\\ &=0 && 1+\gamma\leq\tau\leq\infty. \end{aligned} \tag{3.11}$$

The expression (3.10) for τ_0 is so chosen that

$$\int 4\pi t^2\phi(t)dt=\tfrac{3}{2}\tau_0^3\int\tau^2\Phi(\tau)d\tau=1. \tag{3.12}$$

We now have $\Phi(\tau)$ that satisfies the necessary conditions on the density matrix for single particles: namely from (3.12) it follows that $f(0)=1$ and hence the diagonal element does give the correct number density, and secondly, since Φ lies between zero and two there are only two or fewer electrons in every plane wave single-particle function. In the limit, $\gamma=0$, the function is that for the Single Slater Determinant of minimum energy.

The kinetic energy is now, from (3.8), (3.9), (3.10) and (3.11),

$$\begin{aligned} \epsilon_k&=(9\pi/10)(\pi/3)^{\frac{1}{3}}c^{\frac{2}{3}}(5/2)\tau_0^5\int\tau^4\Phi(\tau)d\tau\\ &=(9\pi/10)(\pi/3)^{\frac{1}{3}}c^{\frac{2}{3}}+(3\pi/2)(\pi/3)^{\frac{1}{3}}c^{\frac{2}{3}}\gamma^2\\ &\quad\times[1+2\gamma^2+\tfrac{1}{5}\gamma^4]^{-5/3}[1+(4/15)\gamma^2+(109/945)\gamma^4\\ &\qquad-(1411/6075)\gamma^6+\cdots]. \end{aligned} \tag{3.13}$$

which becomes ϵ_{0k}, Eq. (1.8) for $\gamma\rightarrow 0$.

The function $f(x)$ is the Fourier transform of $\phi(t)$. Introduce

$$z=(3\pi^2)^{\frac{1}{3}}\tau_0 x,\quad z\tau=2\pi t x, \tag{3.14}$$

and

$$f(x)=F(z), \tag{3.15}$$

where

$$F(z)=\tfrac{3}{2}\tau_0^3z^{-1}\int\tau\Phi(\tau)\,\sin\tau z d\tau. \tag{3.16}$$

After some rather painful manipulation one obtains

$$F(z)=\tau_0^3(1/2\gamma)\int_{1-\gamma}^{1+\gamma}y^4F_0(zy)dy, \tag{3.17}$$

$$F_0(zy)=3(zy)^{-3}[\sin zy-zy\cos zy]. \tag{3.18}$$

Obviously in the limit $\gamma\rightarrow0$ we have $F(z)=F_0(z)$, which is necessary since in this limit one has the Single Slater Determinant solution, $F_0(z)=f_0(x)$, of Eq. (1.15).

4. POTENTIAL ENERGY

In order to compute the potential energy one must evaluate the four integrals, I_2, I_1, $J_2(x_0)$, $J_1(x_0)$, of Eq. (3.3), use I_2 and J_2 to find x_0 from Eq. (3.4), and with x_0, I_1, J_1 use (3.5) for ϵ_p. The operations are reasonably straightforward, but tedious. One ends with Eq. (4.15) expressing ϵ_p as proportional to $c^{\frac{1}{3}}\gamma^{\frac{2}{3}}$ times unity plus a power series of $\gamma^{\frac{2}{3}}$ with numerical coefficients computed for the first two members.

The first integral, I_2, is most simply computed from the Fourier transform Φ, by the use of Eq. (3.7). One finds

$$\begin{aligned}I_2&=1-\frac{1}{2}\int4\pi t^2\phi^2(t)dt=1-\tfrac{3}{4}\tau_0^3\int\tau^2\Phi^2(\tau)d\tau\\&=1-\tau_0^3[1/70\gamma^2][(1+\gamma)^7-(1-\gamma)^7-14\gamma(1-\gamma)^5]\\&=1-[1-\gamma+2\gamma^2-\tfrac{2}{5}\gamma^3+\tfrac{1}{5}\gamma^4+(1/35)\gamma^5]\\&\qquad\times[1+2\gamma^2+\tfrac{1}{5}\gamma^4]^{-1}\\&=\gamma[1+\tfrac{2}{5}\gamma^2+(1/35)\gamma^4][1+2\gamma^2+\tfrac{1}{5}\gamma^4]^{-1},\end{aligned} \tag{4.1}$$

which is zero, as it must be, when $\gamma\rightarrow0$.

To compute I_1, use

$$\begin{aligned}I_1&=\tfrac{3}{2}(3/\pi)^{\frac{1}{3}}-\frac{1}{2}\int4\pi xf^2(x)dx\\&=\tfrac{3}{2}(3/\pi)^{\frac{1}{3}}\left[1-(4/9)\tau_0^{-2}\int zF^2(z)dz\right],\end{aligned} \tag{4.2}$$

and substitute (3.17) for $F(z)$, to find

$$I_1=\frac{3}{2}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\left\{1-\left(\frac{\tau_0^4}{9\gamma^2}\right)\int_{1-\gamma}^{1+\gamma}y^4dy\int_{1-\gamma}^{1+\gamma}x^4dx\times\int_0^\infty dz\,zF_0(xz)F_0(yz)\right\}. \tag{4.3}$$

It is convenient to take double the integral with limits $x\leq y$, namely

$$I_1=\frac{3}{2}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\left\{1-\left(\frac{\tau_0^4}{2\gamma^2}\right)\int_{1-\gamma}^{1+\gamma}y^4dy\int_{1-\gamma}^{y}x^4dx\times\int_0^\infty dz(4/9)zF_0(xz)F_0(yz)\right\}. \tag{4.3$'$}$$

We now make various coordinate transformations. First set $yz=\xi$, $zdz=y^{-2}\xi d\xi$, then use $\zeta=x/y\leq1$, $x^4dx=y^5\zeta^4d\zeta$. The limits on ζ are $y^{-1}(1-\gamma)$ and unity. Finally replace y by $\eta=y^{-1}(1-\gamma)$, $y^7dy=-(1-\gamma)^8\eta^{-9}d\eta$, with limits unity and $(1-\gamma)/(1+\gamma)=1-2\gamma/(1+\gamma)$. The limits on ζ are now η and unity. The expression is

$$I_1=\frac{3}{2}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\left\{1-\frac{\tau_0^4}{2\gamma^2}(1-\gamma)^8\int_{1-\epsilon}^{1}d\eta\,\eta^{-9}\int_\eta^1d\zeta\zeta^4\times\int_0^\infty d\xi\left[\frac{4}{9}\xi F_0(\xi)F_0(\zeta\xi)\right]\right\}, \tag{4.3$''$}$$

with $\epsilon=2\gamma(1+\gamma)^{-1}$. The integral,

$$\theta(\zeta)=\zeta^4\int_0^\infty d\xi\left[\frac{4}{9}\xi F_0(\xi)F_0(\zeta\xi)\right], \tag{4.4}$$

is found by direct integration to be

$$\begin{aligned}\theta(\zeta)&=\tfrac{1}{2}\zeta^4+\tfrac{1}{2}\zeta^2-\tfrac{1}{4}\zeta(1-\zeta^2)^2\ln[(1+\zeta)/(1-\zeta)]\\&=-\sum_{\nu\geq0}[4/(2\nu-1)(2\nu+1)(2\nu+3)]\zeta^{2\nu+4}.\end{aligned} \tag{4.5}$$

This can be integrated to give

$$\begin{aligned}&\int_\eta^1\theta(\zeta)d\zeta=\Theta(\eta)\\&=(1/36)\left\{8+3\eta-8\eta^3-3\eta^5-\tfrac{3}{2}(1-\eta^2)^3\ln\frac{1+\eta}{1-\eta}\right\}.\end{aligned} \tag{4.6}$$

Setting $\epsilon=2\gamma(1+\gamma)^{-1}$, $1-\epsilon=(1-\gamma)(1+\gamma)^{-1}$, one finds

$$J(x)=\int_x^1d\eta\eta^{-9}\Theta(\eta),$$

$$\begin{aligned}J[(1-\gamma)(1+\gamma)^{-1}]&=2\gamma^2(1-\gamma)^{-8}\{1+(\gamma^2/18)\\&\qquad\times[35+10\gamma^2+91\gamma^4-12\ln(\gamma^{-1})]\}.\end{aligned} \tag{4.7}$$

Finally, with Eq. (3.9) for τ_0, one finds that

$$I_1=(3/\pi)^{\frac{1}{3}}\gamma^2[\ln(\gamma^{-1})+1.0833]+O(\gamma^4). \tag{4.8}$$

To compute $J_2(x_0)$ and $J_1(x_0)$ of Eq. (3.3) we assume x_0 to be small and find the asymptotic expansion of $F(z)$, Eq. (3.17) for small z to be

$$\begin{aligned}F(z)=1-(1/10)[1+3\gamma^2-\cdots]z^2+(1/280)z^4\\-(1/15\,120)z^6+\cdots,\end{aligned} \tag{4.9}$$

and with (3.14), (3.15),

$$f^2(x)=1-(1/5)(3\pi^2)^{\frac{2}{3}}[1+(5/3)\gamma^2+\cdots]x^2 \\ +(3/175)(3\pi^2)^{4/3}x^4-(4/4725)(3\pi^2)^2x^6+\cdots. \quad (4.10)$$

Using this in (3.3) one has

$$J_2=(6\pi^2/25)(\pi/3)^{\frac{1}{3}}[1+(5/3)\gamma^2+\cdots]x_0^5 \\ -(18\pi^4/1225)(3/\pi)^{\frac{1}{3}}x_0^7+(8\pi^5/4725)x_0^9-\cdots, \quad (4.11)$$

$$J_1=(3\pi^2/10)(\pi/3)^{\frac{1}{3}}[1+(5/3)\gamma^2+\cdots]x_0^4 \\ -(3\pi^4/175)(3/\pi)^{\frac{1}{3}}x_0^6. \quad (4.12)$$

In these employ the zeroth-order expression, Eq. (3.4′), $(2\pi x_0^3/3)=I_2$, with I_2 from (4.1), to obtain a zeroth-order approximation for J_2, and continue to iterate. One finds

$$x_0^3=(3/2\pi)\gamma(1+2\gamma^2+\tfrac{1}{5}\gamma^4)^{-1}[1-0.70160\gamma^{\frac{2}{3}} \\ +1.0715\gamma^{4/3}-1.512\gamma^{6/3}+\cdots]. \quad (4.13)$$

With this, in (4.12) for J_1 one has

$$J_1=(9\pi/20)2^{-\frac{1}{3}}\gamma^{4/3}[1-1.20063\gamma^{\frac{2}{3}}+\cdots]. \quad (4.14)$$

One now has the necessary quantities, x_0 from (4.13), J_1 of (4.14), and I_1 of (4.8) to compute $\Delta\epsilon_p$ from (3.5). The leading term is seen to be that due to x_0^2, proportional to $\gamma^{\frac{2}{3}}$, which alone was used in Sec. 3 to obtain the "best" analytical form for $f(x)$. We find

$$\epsilon_p=\epsilon_{0p}-\tfrac{3}{4}(2\pi/3)^{\frac{1}{3}}c^{\frac{1}{3}}\gamma^{\frac{2}{3}}[1+2\gamma^2+\tfrac{1}{5}\gamma^4]^{-\frac{2}{3}}F(\gamma), \quad (4.15)$$

where

$$F(\gamma)=\gamma^{-\frac{2}{3}}[1+2\gamma^2+\tfrac{1}{5}\gamma^4]^{\frac{2}{3}} \\ \times[(2\pi x_0^3/3)^{\frac{2}{3}}+\pi^{-1}(2\pi/3)^{\frac{2}{3}}(J_1-I_1)] \\ =1+0.11693\gamma^{\frac{2}{3}}-0.5982\gamma^{4/3} \\ -0.51311\gamma^{4/3}\ln(\gamma^{-1}). \quad (4.15')$$

5. ENERGY MINIMIZATION

Set

$$\gamma^{\frac{2}{3}}=\beta \quad (5.1)$$

and the kinetic energy, ϵ_k, Eq. (3.13) is

$$\epsilon_k=\epsilon_{0k}+4.78539c^{\frac{2}{3}}\beta^3[1+2\beta^3+0.2\beta^6]^{-5/3}K(\beta), \quad (5.2)$$

$$K(\beta)=1+0.26667\beta^3+0.11534\beta^6 \\ -0.23226\beta^9+\cdots. \quad (5.2')$$

The potential energy from Eq. (4.15) is

$$\epsilon_p=\epsilon_{0p}-0.959579c^{\frac{1}{3}}\beta[1+2\beta^3+0.2\beta^6]^{-\frac{2}{3}}P(\beta), \quad (5.3)$$

$$P(\beta)=1+0.1169\beta-0.5982 \\ -0.7696\beta^2\ln(\beta^{-1})+\cdots. \quad (5.3')$$

Differentiation of the sum with respect to β gives zero when

$$\beta=0.25854c^{-1/6}[P+dP/d\ln\beta]^{\frac{1}{2}}, \quad (5.4)$$

plus terms of order β^3. From the zeroth-order approximation, $\beta=0.258c^{-1/6}$, one sees that with $c\cong 1/27$, or one electron per three Bohr radii cubed, one has β equal to about one-half. The correction terms are significant at these low densities. Using (5.3′) for $P(\beta)$, and replacing $\ln(\beta^{-1})$ by the zeroth-order approximation, $\ln(\beta^{-1})=\frac{1}{6}\ln c+1.35274$, one finds

$$\beta=0.25854c^{-1/6}\{1+0.1169 \\ -[2.0805+0.19241\ln c]\beta^2+\cdots\} \\ =0.25854c^{-1/6}\{1+0.0302c^{-1/6} \\ -[0.1381+0.01286\ln c]c^{-\frac{1}{3}}+\cdots\}. \quad (5.5)$$

6. RESULTS

Enter (5.2) for the kinetic energy and (5.3) for the potential energy with (5.5) for β. One obtains

$$\begin{aligned}\epsilon_{0k}&=\ 2.87123c^{\frac{2}{3}}\text{ atomic units,}\\ &=78.134\quad c^{\frac{2}{3}}\text{ ev,}\end{aligned} \quad (6.1)$$

$$\begin{aligned}\Delta\epsilon_k&=\ 0.08269c^{1/6}k(c)\text{ atomic units}\\ &=\ 2.250\quad c^{1/6}k(c)\text{ ev,}\end{aligned} \quad (6.2)$$

$$k(c)=[1+0.0346c^{-\frac{1}{2}}]^{-5/3}\{1+0.0907c^{-1/6} \\ -[0.4117+0.0386\ln c]c^{-\frac{1}{3}}\} \\ \times[1+0.0046c^{-\frac{1}{2}}+\cdots], \quad (6.2')$$

$$\begin{aligned}\epsilon_{0p}&=-\ 0.73856c^{\frac{1}{3}}\text{ atomic units}\\ &=-20.098\quad c^{\frac{1}{3}}\text{ ev,}\end{aligned} \quad (6.3)$$

$$\begin{aligned}\Delta\epsilon_p&=-\ 0.24890c^{1/6}p(c)\text{ atomic units}\\ &=-\ 6.751\quad c^{1/6}p(c)\text{ ev,}\end{aligned} \quad (6.4)$$

$$p(c)=[1+0.03456c^{-\frac{1}{2}}]^{-\frac{2}{3}}[1+0.0604c^{-1/6} \\ -(0.2459+0.0214\ln c)c^{-\frac{1}{3}}+\cdots]. \quad (6.4')$$

The total correlation energy is

$$\begin{aligned}\Delta\epsilon_c&=-0.16540c^{1/6}[\tfrac{1}{2}k(c)+\tfrac{1}{2}p(c)]\text{ atomic units,}\\ &=-4.500\quad c^{1/6}[\tfrac{1}{2}k(c)+\tfrac{1}{2}p(c)]\text{ ev.}\end{aligned} \quad (6.5)$$

In these equations c, of Eq. (1.6) is the concentration of electrons per cubic Bohr radius,

$$c=0.1481\times\text{number of electrons per (angstrom)}^3. \quad (6.6)$$

The distance, x_0, out to which $k(x)$ is unity is given by (4.11) as

$$x_0=0.39742c^{-\frac{1}{2}}[1-0.1502c^{-1/6}+\cdots], \quad (6.7)$$

which is measured in such units that the number density is unity. The volume, v_0, occupied by this "hole" around each electron is then

$$v_0=(4\pi/3)x_0^3=0.26283c^{-\frac{1}{4}}[1-0.4506c^{-1/6}+\cdots], \quad (6.7'')$$

measured in units of the volume per electron in the gas.

The momentum distribution of the electrons is determined by $\Phi(\tau)$ of Eq. (3.11), with τ related to momentum by (3.9) and $\gamma^{\frac{2}{3}}=\beta$. For the Single Slater Determinant all momentum states up to

$$|\mathbf{p}|=p_0=(3/8\pi)^{\frac{1}{3}}h\rho_0^{\frac{1}{3}} \quad (6.8)$$

are filled with two electrons each. For the "correlated" system the momentum states up to

$$|\mathbf{p}|_l = p_0(1-\beta^{\frac{2}{3}})(1+2\beta^3+0.2\beta^6)^{-\frac{1}{3}} \cong p_0(1-0.1314c^{-\frac{1}{4}}) \tag{6.9}$$

are filled with two electrons each, and all above

$$|\mathbf{p}|_u \cong p_0(1+0.1314c^{-\frac{1}{4}}) \tag{6.9'}$$

are empty. The number per state decreases monotonically from 2 to 0 with a term proportional to $|\mathbf{p}|^2$ between $|p|_l$ and $|p|_u$.

To obtain some idea of the range of applicability of the equations we may try them with the alkalis. If one considers the valence electron alone, so that one treats only one electron per atom, the concentration c is lowest for cesium than for any other metal, and is generally low in the alkalis.

For cesium one has

$$c=0.001256, \quad \text{Cs, one electron,}$$
$$\beta=0.7870[1+0.092-0.483+\cdots].$$

The convergence of the series approximation (5.5) for β is obviously nonexistent at these low concentrations. For $k(c)$ and $p(c)$ the convergence is equally bad, and direct calculation with the equations given leads to an expression for $\Delta\epsilon_p$ which is greater in magnitude than the value $0.637\epsilon_{0p}$ found from Eq. (1.18) as the lowest possible reduction in potential energy due to electron correlation.

However for lithium, with

$$c=0.00686, \quad \text{Li, one electron,}$$
$$\beta=0.5931[1+0.069-0.390+\cdots],$$

there is some sign of nearing convergence.

The general integrations given in Sec. 4 are actually adequate even for the low density examples quoted. Equation (4.1) for I_2 is exact. Even with the maximum possible value of x_0, $x_0^3=3/4\pi$, the quantity J_2 is given by (4.11) adequately. The evaluation of x_0 is then awkward, but possible, and the other integrals are satisfactorily given.

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Cadmium Sulfide with Silver Activator

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Further experimental evidence is presented in connection with a model which has been proposed by Lambe and Klick for CdS(Ag). In this model, the silver activator is assumed to give rise to a level which is approximately 0.4 ev below the conduction band, and that luminescence occurs when an electron in such an activator level recombines with a free hole. It is shown that irradiation in the 1μ infrared region stimulates luminescence by generating free holes, while also causing well known quenching effects in photocurrent. It is also shown that 3μ irradiation gives rise to photoconduction by exciting electrons from the activator levels into the conduction band. The proposed model indicates that irradiation in the 3μ region should quench luminescence by removing electrons from activator levels, and this is found experimentally. These experiments further substantiate the proposed model for CdS(Ag).

I. INTRODUCTION

IN a recent paper[1] (referred to as LK), a model for CdS(Ag) was discussed based on observations of infrared stimulation of photocurrent and luminescence and on relationships observed between photoconductivity and luminescence. The essential point of this model was that silver activation in CdS gave rise to an activator level about 0.4 ev below the conduction band (see Fig. 1). It was assumed that luminescence occurs when an electron in this level recombines with a free hole. This model differs from earlier models[2,3] for sulfide phosphors in the position of this activator level. It had previously been assumed that the activator level was just above the valence band, and that luminescence occurred when a free electron returned to this level from the conduction band. The purpose of this paper is to report further experimental evidence which relates to the model proposed in LK for CdS(Ag).

The cadmium sulfide crystals used in these experiments were activated by first immersing them in a 0.5N solution of $AgNO_3$ for approximately 30 seconds and then, after washing with distilled water and drying, firing at 800°C for one hour in a helium atmosphere. All experiments here were done at 77°K and temperature control was obtained by direct immersion of the crystals in liquid nitrogen.

II. EFFECTS OF 1μ IRRADIATION ON PHOTOCONDUCTION AND LUMINESCENCE

In LK, experimental evidence was presented showing separately the effects of 1μ irradiation on luminescence and photoconduction. The 1μ irradiation produced a

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