

Short-range correlations and the structure factor and momentum distribution of electrons

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1975 J. Phys. A: Math. Gen. 8 1513

(<http://iopscience.iop.org/0305-4470/8/9/021>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.88

The article was downloaded on 02/06/2010 at 05:11

Please note that [terms and conditions apply](#).

Short-range correlations and the structure factor and momentum distribution of electrons

J C Kimball

Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803, USA

Received 15 April 1975

Abstract. It is shown that for any system of non-relativistic electrons and nuclei the large-wavevector limit of the probability of finding an electron with momentum $\hbar k$ is proportional to $1/k^8$, and the electronic structure factor is proportional to $1/k^4$. Furthermore, the coefficient of the $1/k^4$ term in the structure factor is proportional to the zero separation electron-electron correlation. The coefficient of the $1/k^8$ term in the momentum distribution is proportional to the sum of zero-range electron-electron and electron-nuclear correlations.

1. Introduction

Two important properties of many-electron systems are the structure factor, $S(\mathbf{q})$, and the distribution of the electrons' momenta. The momentum distribution is given in terms of $n(\mathbf{k})$, the probability of finding an electron with momentum $\hbar k$, and $S(\mathbf{q})$ is the Fourier transform of the two-electron correlation function.

In principle, both $n(\mathbf{k})$ and $S(\mathbf{q})$ are physically observable. The Born approximation to the elastic plus inelastic cross section for scattering with wavevector \mathbf{q} from these electrons is proportional to $S(\mathbf{q})$ (Nozieres 1964, Inokuti 1971). Information on the momentum distribution of the electrons can be obtained from positron annihilation data (Stewart and Roellig 1967) and from Compton scattering experiments when the impulse approximation is valid (Eisenberger *et al* 1972). Theoretically, $n(\mathbf{k})$ and $S(\mathbf{q})$ can only be approximated even for idealized systems like the uniform density electron gas. An exact knowledge of these important quantities would, for example, enable one to calculate the kinetic and mutual interaction energies of the electrons.

The purpose of this paper is to point out that the large-wavevector limits of $n(\mathbf{k})$ and $S(\mathbf{q})$ can be expressed in terms of the zero-range electron-electron and electron-nuclear correlations. In principle, then, measurements like scattering cross sections which yield information of $S(\mathbf{q})$ and $n(\mathbf{k})$ also provide a measure of the interparticle correlations. These relations are general, and they apply to any system (atoms, molecules, or condensed matter) of N non-relativistic electrons interacting only through Coulomb forces with each other and \mathcal{N} nuclei. For simplicity the nuclei will be assumed static since nuclear motion would not significantly alter the results. The basic idea of the calculation is simple; when any two particles are sufficiently close together, their interaction dominates the problem and the basic physics can be obtained from a two-particle Schrödinger equation. This approach has been applied previously (Kimball 1973) in an investigation of $S(\mathbf{q})$ and the dielectric response of the electron gas. Here the method is extended to

real systems and the momentum distribution is also calculated. Mathematically stated, $n(\mathbf{k})$ and $S(\mathbf{q})$ are obtained as Fourier transforms of functions bilinear in the many-electron wavefunction. This wavefunction is continuous, and its derivative is continuous except at points in phase space which correspond to zero interparticle separation. The large-wavevector dependences of $n(\mathbf{k})$ and $S(\mathbf{q})$ are completely determined by the non-analytic points of the wavefunction.

The Hamiltonian for the electrons is

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - e^2 \sum_{i=1}^N \sum_{l=1}^N \frac{Z_l}{|\mathbf{r}_i - \mathbf{R}_l|} + e^2 \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

where \mathbf{r}_i and \mathbf{R}_l are the electronic and nuclear coordinates, ∇_i^2 means differentiation with respect to \mathbf{r}_i and eZ_l is the charge of the l th nucleus. The eigenstates of H are time-independent wavefunctions $\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)$. This wavefunction is assumed to be normalized in a box of volume V with periodic boundary conditions, and spin indices have been suppressed. The following quantities can all be expressed in terms of the wavefunction.

(i) $\rho(\mathbf{r}; \mathbf{r}')$ is the single electron density matrix :

$$\rho(\mathbf{r}; \mathbf{r}') = N \int \psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_N) \prod_{i=2}^N d\mathbf{r}_i$$

The real-space particle density is

$$n(\mathbf{r}) = \rho(\mathbf{r}; \mathbf{r}).$$

(ii) $n(\mathbf{k})$ is the probability of finding an electron with wavevector \mathbf{k} :

$$n(\mathbf{k}) = \frac{N}{V} \int \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')] \psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r} d\mathbf{r}' \prod_{i=2}^N d\mathbf{r}_i$$

where \mathbf{k} must take on values consistent with the periodic boundary conditions.

(iii) $g(\mathbf{r}_1, \mathbf{r}_2)$ is the probability of finding a pair of electrons at points \mathbf{r}_1 and \mathbf{r}_2 :

$$g(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int \psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \prod_{i=2}^N d\mathbf{r}_i.$$

The pair correlation function $g(\mathbf{r})$ is the probability of finding particles separated by a distance \mathbf{r} :

$$g(\mathbf{r}) = \int g(\mathbf{r}_1 + \mathbf{r}, \mathbf{r}_1) d\mathbf{r}_1$$

and the structure factor is the Fourier transform of $g(\mathbf{r})$

$$S(\mathbf{q}) = \int e^{-i\mathbf{q} \cdot \mathbf{r}} g(\mathbf{r}) d\mathbf{r}.$$

For condensed matter systems which occupy all of the volume, V , the structure factor will be proportional to V^2 when $\mathbf{q} = 0$. If the system is periodic, $S(\mathbf{q})$ will also diverge as V^2 when \mathbf{q} is a reciprocal lattice vector. In this case, we are concerned with values of \mathbf{q} not equal to a reciprocal lattice vector so that $S(\mathbf{q})$ is only proportional to the volume.

2. The structure factor

The large- q behaviour of $S(q)$ is determined by the small- r dependence of $g(r)$. As r approaches zero the dynamics of the two adjacent particles is dominated by their Coulomb repulsion. Writing $\psi(r_1, r_2, r_3, \dots, r_N)$ as $\tilde{\psi}(r)$ where $r = (r_1 - r_2)$, $R = (r_1 + r_2)/2$ and the coordinates $\{R, r_3, \dots, r_N\}$ have been dropped, the Schrödinger equation becomes

$$\left(-\frac{\hbar^2}{2\mu} \nabla_r^2 + \frac{e^2}{|r|} \right) \tilde{\psi}(r) = (E - H') \tilde{\psi}(r)$$

where μ is the reduced mass of the two-electron pair ($\mu = \frac{1}{2}m$), E is the energy, and H' contains the remaining terms in the Hamiltonian. Because $(E - H')$ is non-singular as r approaches zero, it is unimportant for small r . Significant contributions to the short-range correlations occur only when the two electrons are in a relative singlet state with zero angular momentum. To first order in r , solutions to the Schrödinger equation must be of the form

$$\tilde{\psi}(r) = f(R, r_3, \dots, r_N) \left(1 + \frac{|r|}{2a_0} + \dots \right)$$

where a_0 is the first Bohr radius (\hbar^2/me^2). The ratio of $\partial g(r)/\partial |r|$ to $g(r)$ as r approaches zero can be obtained by an integration of $\psi^* \psi$ over the coordinates $\{R, r_3, \dots, r_N\}$. The result is

$$\left. \frac{\partial g(r)}{\partial |r|} \right|_{r \rightarrow 0} = \frac{g(0)}{a_0}.$$

Because the gradient of the two-electron correlation function is discontinuous at the origin, its Fourier transform, $S(q)$, must approach $8\pi(\partial g(r)/\partial |r|)|_{r \rightarrow 0}/q^4$ for large q . This can easily be shown by writing

$$g(r) = -\left. \frac{\partial g(r)}{\partial |r|} \right|_{r \rightarrow 0} \left(\frac{1}{\gamma} e^{-\gamma|r|} \right) + \tilde{g}(r)$$

where $\tilde{g}(r)$ has a continuous derivative at $r = 0$. The asymptotic form of the Fourier transform of the first term gives $8\pi(\partial g(r)/\partial |r|)|_{r \rightarrow 0}$ times $1/q^4$ independent of γ , and because $\tilde{g}(r)$ is smooth, its Fourier transform vanishes more rapidly than $1/q^4$ as $q \rightarrow \infty$. Hence,

$$\lim_{|q| \rightarrow \infty} (q^4 S(q)) = \frac{8\pi}{a_0} g(0).$$

This direct two-electron correlation is the only effect which leads to terms in $S(q)$ as large as $1/q^4$ for large q . The electrons tend to pile up near nuclear positions, and there is a peak in $g(r_1, r_2)$ at points where r_1 and r_2 approach the nuclear coordinates. However, the integration over the centre of mass coordinate necessary to obtain $g(r)$ from $g(r_1, r_2)$ smooths out this peak so that there are no other points where the gradient of $g(r)$ is discontinuous.

3. The momentum distribution

The large-momentum limit of $n(k)$ reflects discontinuous derivatives of the many-electron wavefunction rather than the correlation function. Kinks in the wavefunction occur whenever two electrons approach each other and whenever an electron approaches

a nucleus. These two contributions to $n(\mathbf{k})$ for large \mathbf{k} are additive. The term arising from small electron–nuclear separation will be considered first.

By picking a coordinate system centred on the l th nucleus, and suppressing indices so that $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ becomes $\tilde{\psi}(\mathbf{r})$ (the coordinate \mathbf{r}_1 is changed to \mathbf{r}), the Schrödinger equation can be written as

$$\left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 - \frac{Z_l e^2}{|\mathbf{r}|} \right) \tilde{\psi}(\mathbf{r}) = (E - H') \tilde{\psi}(\mathbf{r}).$$

The terms in the Hamiltonian which are non-singular as \mathbf{r} approaches zero are contained in H' . As before, to first order in \mathbf{r} , $\tilde{\psi}(\mathbf{r})$ must be of the form

$$\tilde{\psi}(\mathbf{r}) = f(\mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \left(1 - \frac{Z_l |\mathbf{r}|}{a_0} + \dots \right).$$

Since $n(\mathbf{k})$ is obtained from a double Fourier transform of $\tilde{\psi}^*(\mathbf{r})\tilde{\psi}(\mathbf{r}')$, the dominant nuclear contribution to $n(\mathbf{k})$ ($=n(\mathbf{k})_{\text{nuc}}$) occurs when both \mathbf{r} and \mathbf{r}' are near a nucleus. If \mathbf{r} is near \mathbf{R}_l and \mathbf{r}' is near \mathbf{R}_m , then

$$\rho(\mathbf{r}; \mathbf{r}') \simeq \rho(\mathbf{R}_l; \mathbf{R}_m) \left(1 - \frac{Z_l |\mathbf{r} - \mathbf{R}_l|}{a_0} \right) \left(1 - \frac{Z_m |\mathbf{r}' - \mathbf{R}_m|}{a_0} \right).$$

Taking the Fourier transform yields the asymptotic form of $n(\mathbf{k})_{\text{nuc}}$

$$n(\mathbf{k})_{\text{nuc}} \simeq \left(\frac{8\pi}{a_0} \right)^2 \frac{1}{V k^8} \sum_{lm} \exp[i\mathbf{k} \cdot (\mathbf{R}_l - \mathbf{R}_m)] Z_l Z_m \rho(\mathbf{R}_l; \mathbf{R}_m).$$

This separates into diagonal ($l = m$) and non-diagonal terms. The non-diagonal terms oscillate and average to zero for large \mathbf{k} . The important diagonal contribution to $n(\mathbf{k})_{\text{nuc}}$ means that

$$\lim_{|\mathbf{k}| \rightarrow \infty} (k^8 \overline{n(\mathbf{k})_{\text{nuc}}}) = \left(\frac{8\pi}{a_0} \right)^2 \frac{1}{V} \sum_l Z_l^2 n(\mathbf{R}_l)$$

where the bar indicates an average over a range of \mathbf{k} values large compared with the inverse of the nearest-neighbour nuclear distance.

The electronic contribution to $n(\mathbf{k})$ ($=n(\mathbf{k})_{\text{el}}$) for large \mathbf{k} is produced by the kink in the wavefunction at zero interelectronic separation. The integrand of

$$n(\mathbf{k}) = \frac{N}{V} \int \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')] [\psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_N)] \mathbf{d}\mathbf{r} \mathbf{d}\mathbf{r}' \prod_{i=2}^N \mathbf{d}\mathbf{r}_i$$

will have kinks whenever \mathbf{r} or \mathbf{r}' equals any of the coordinates $\{\mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N\}$. However, if both \mathbf{r} and \mathbf{r}' are not near the same electronic coordinate (say \mathbf{r}_2) the integration over $\prod_{i=2}^N \mathbf{d}\mathbf{r}_i$ introduces additional factors of $1/k^2$. The asymptotic term is thus determined by

$$n(\mathbf{k}) \rightarrow \frac{N(N-1)}{V} \int_{\Omega(\mathbf{r}_2)} \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')] \psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi(\mathbf{r}', \mathbf{r}_2, \dots, \mathbf{r}_N) \mathbf{d}\mathbf{r} \mathbf{d}\mathbf{r}' \prod_{i=2}^N \mathbf{d}\mathbf{r}_i$$

where $\int_{\Omega(\mathbf{r}_2)}$ means \mathbf{r} and \mathbf{r}' are near \mathbf{r}_2 and the factor $(N-1)$ occurs because only one coordinate (\mathbf{r}_2) was chosen. Integration over \mathbf{r} and \mathbf{r}' yields

$$n(\mathbf{k})_{\text{el}} \rightarrow \left(\frac{4\pi}{a_0} \right)^2 \frac{1}{k^8} \frac{N(N-1)}{V} \int \psi^*(\mathbf{r}_2, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \psi(\mathbf{r}_2, \mathbf{r}_2, \dots, \mathbf{r}_N) \prod_{i=2}^N \mathbf{d}\mathbf{r}_i$$

or

$$\lim_{|\mathbf{k}| \rightarrow \infty} (k^8 n(\mathbf{k})_{\text{el}}) = \left(\frac{4\pi}{a_0}\right)^2 \frac{g(0)}{V}$$

Summing the electronic and nuclear contributions to $n(\mathbf{k})$ for large \mathbf{k} , and averaging over a range of \mathbf{k} vectors greater than the inverse nuclear separation gives the final result

$$\lim_{|\mathbf{k}| \rightarrow \infty} (k^8 \overline{n(\mathbf{k})}) = \left(\frac{4\pi}{a_0}\right)^2 \frac{1}{V} \left(g(0) + 4 \sum_I n(\mathbf{R}_I) Z_I^2 \right).$$

4. Discussion

For atoms $g(0)$ is of order $Z(Z-1)/v$ (where v is the 'volume' of the atom) times a number that is probably considerably less than 1. But, $n(\mathbf{R})$ is of order Z/v times a number somewhat greater than 1. This means that the electronic correlation correction to $n(\mathbf{k})$ for large \mathbf{k} is small compared to the nuclear term. It might be a few per cent for helium and should decrease as Z increases. On the other hand, the large- q dependence of the structure factor is completely determined by the electron-electron correlations, and its measurement could be used as a check of many-electron wavefunctions. Qualitatively similar conclusions about the relative importance of nuclear and electronic contributions to $n(\mathbf{k})$ for large \mathbf{k} apply as well to molecules and condensed matter. In principle it would be possible to observe changes in interelectron correlations in going from individual molecules to condensed matter by observing the large- q limit of $S(q)$, but in practice the change would probably be small.

From a theoretical point of view, the uniform density electron gas is often studied as a model of a metal. For this model, there is no contribution to $n(\mathbf{k})$ from nuclear terms and

$$V \left(\frac{a_0}{4\pi}\right)^2 \lim_{|\mathbf{k}| \rightarrow \infty} (k^8 n(\mathbf{k})) = \left(\frac{a_0}{8\pi}\right) \lim_{|q| \rightarrow \infty} (q^4 S(q)) = g(0).$$

Others have observed that $n(\mathbf{k})$ should go as $1/k^8$ for large \mathbf{k} , but have not noted that the coefficient is proportional to the zero-range correlation (Eisenberger *et al* 1972, Daniel and Vosko 1960). Our results can be compared with those of Daniel and Vosko if it is noted that the $n(\mathbf{k})$ used here is the sum of the spin-up and spin-down probabilities. Then using the units of Daniel and Vosko ($\hbar = m = 1$ and k expressed in units of k_F), we find that the results agree only if the zero-range correlation function, $g(0)$, has the Hartree-Fock value of $1/2(N/V)^2$. Higher-order terms in a Gell-Mann-Brueckner-type expansion of $n(\mathbf{k})$ must yield additional terms proportional to $1/k^8$ which reflect variations of $g(0)$ from its Hartree-Fock value.

References

- Daniel E and Vosko S H 1960 *Phys. Rev.* **120** 2041-4
 Eisenberger P, Lam L, Platzman P M and Schmidt P 1972 *Phys. Rev. B* **6** 3671-81
 Inokuti M 1971 *Rev. Mod. Phys.* **43** 297-347
 Kimball J C 1973 *Phys. Rev. A* **7** 1648-52
 Nozieres P 1964 *Interacting Fermi System* (New York: Benjamin) pp 50-5
 Stewart A T and Roellig L O (eds) 1967 *Positron Annihilation* (New York: Academic Press)