

ELECTRON CORRELATION IN MOLECULAR GROUND STATES: SOME EXPERIMENTAL ASPECTS

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ABSTRACT

Experimental results on correlation effects on the ground state structures of molecules are surveyed. Both direct measurements of charge and momentum densities as well as other indirect measurements are critically examined. It is shown that recent electron and x-ray scattering experiments from gas targets are capable of yielding very sensitive data on the effects of electron correlation.

INTRODUCTION

Theoretical descriptions of molecular structure have long centered on the electron charge density¹. Even with modern high speed computers theorists have sought ways to avoid the computation of many electron wave functions by attempting to construct the charge density directly². Chemists have attempted to relate chemical reactivity to the details of ground state electron charge and momentum densities³.

All of this is not so surprising if one notes that for any bound state of a many electron system the total electronic energy is determined by the one electron charge density, $\rho(\vec{r})$, and the electron pair correlation function, $P(r_{12})$ or, equivalently, the spherically averaged momentum density, $p(p)$ ⁴. In addition most ground state properties can be computed from a knowledge of these densities. Because of the central importance of these density functions we will limit this review to experiments capable of providing information on the densities themselves (direct observations) or the observed properties derived from these densities (indirect observations). Further, since theoretical calculations can generally be carried out faster and more cheaply than experiments we will further limit ourselves to those experiments providing detail that is equal to or beyond the present capability of computational methods. In this way different and very strenuous tests can be provided for the development of new theoretical approaches.

Molecular structure calculations have been carried out by a variety of methods, both *ab initio* and empirical⁵. Perhaps the most utilized *ab initio* approach is the Hartree-Fock (HF) method⁶. The problem posed is: What is the lowest total electronic energy for a given bound state achievable using an orbital picture of the molecule, one orbital per electron with a trial wave function which rigorously satisfies all the boundary conditions of the problem? This question has a unique mathematical answer and pro-

vides us with a theoretical bench mark for comparison with experiment and other theoretical approaches. The HF method often provides an excellent description of structure and properties although in some cases it may provide erroneous results⁷. Theoreticians, because the HF approximation is well defined, have labeled the difference between the exact value of the total electronic energy, corrected for relativistic contributions, and the HF energy as the correlation energy. The word correlation would seemingly signify the influence of the motion of one molecular electron upon others and, of course, a certain amount of such correlation is built into the HF approach by forcing the HF wave function to satisfy all the boundary conditions of the problem such as the Pauli exclusion principle¹⁵. Hence, we must keep in mind that the definition of correlation energy is a mathematical and not a physical one. Correlation means the additional influence of a molecular electron upon its neighbors beyond that provided for in the HF approximation. In this article we will extend the definition of correlation to the densities of interest as well as the properties derivable from them. The correlation effect on a density will be the difference between the exact (experimental) density and the HF density.

Because we will focus on the structure of individual molecules we will further restrict our coverage to experiments conducted in the gas phase in order to avoid perturbations to the relevant densities due to neighboring molecules. This means that any discussion of correlation effects on the spin density which is also a quantity of great interest, will be omitted since these measurements are generally carried out on solids. Also, spectral information, excepting certain global spectroscopic quantities with no dependence on the excited state, will be omitted from discussion. Finally, in keeping with our goal of only considering experiments which push current computational methods to their very limit, we will only consider those experiments and measured quantities which within experimental error can actually document significant variations from the HF predictions.

DIRECT EXPERIMENTAL OBSERVATION OF CORRELATION EFFECT

In the late twenties and early thirties the use of x-rays to obtain charge densities was introduced⁸. It was not until the 50's that electrons were also used for this purpose⁹. The connection between charge densities and

scattering experiments is made by use of the Born approximation for x-ray scattering¹⁰ and the Born-Bethe theory of electron scattering¹¹. These theories, when experiments are performed within their range of validity, provide direct information by relating the scattered intensities to Fourier transforms of the densities themselves.

It will be convenient to define normalized intensities which are independent of the method used to obtain them. In simplest terms, using the theories in a form already known in the early 30's, we may define normalized x-ray (XR), and electron (EL), scattering intensities as¹²

$$I_{\text{XR,EL}} = (d\sigma/d\Omega)_{\text{XR,EL}} / (d\sigma/d\Omega)^{\text{T,M}} \quad (1)$$

where $d\sigma/d\Omega$ is the differential cross section and T signifies the Thompson cross section for the scattering of an x-ray by a single electron and M stands for the Mott cross section for the scattering of an electron by a single electron. We will employ the subscripts TOT, E and I on normalized intensities to denote the total, elastic (coherent) and inelastic (incoherent) scattering respectively. The normalized intensities for all possible scattering experiments, involving a single detector, that can be carried out are

$$I_{\text{TOT}}^{\text{XR}} = N + \left\langle \int_0^\infty dr_{12} P(r_{12}) j_0(Kr_{12}) \right\rangle_{\text{vib}} \quad (2)$$

$$I_{\text{E}}^{\text{XR}} = \left\langle \int dr p(\vec{r}) \int dr' p(\vec{r}') j_0(K|\vec{r}-\vec{r}'|) \right\rangle_{\text{vib}} \quad (3)$$

$$I_{\text{I}}^{\text{XR}} = I_{\text{T}}^{\text{XR}} - I_{\text{E}}^{\text{XR}} \quad (4)$$

$$I_{\text{TOT}}^{\text{EL}} = \sum_{n=1}^M Z_n \sum_{m=1}^M Z_m \left\langle j_0(KR_{nm}) \right\rangle_{\text{vib}} \quad (5)$$

$$-2 \sum_{n=1}^M Z_n \left\langle \int dr p(\vec{r}) j_0(K|\vec{r}-\vec{R}_n|) \right\rangle_{\text{vib}} + I_{\text{TOT}}^{\text{XR}} \quad (5)$$

$$I_{\text{E}}^{\text{EL}} = I_{\text{TOT}}^{\text{EL}} - I_{\text{I}}^{\text{XR}} \quad (6)$$

$$I_{\text{I}}^{\text{EL}} = I_{\text{I}}^{\text{XR}} \quad (7)$$

where K is the momentum transferred to the target by the projectile particle, $j_0(x)$ is the zero order spherical Bessel function $(\sin x)/x$, Z_n is the nuclear charge of a nucleus located at the point \vec{R}_n with respect to the principal axis center of mass coordinate system in a molecule containing N electrons and M nuclei, \vec{R}_{nm} is the distance between the nth and mth nuclei and $\langle \rangle_{\text{vib}}$ signifies an average over the vibrational motion of the electronic ground state of the molecule. Note that the average over the rotational motion of the molecule has already been carried out¹³.

It is important to point out that the various x-ray and electron experiments are complementary and their results can be predicted by a knowledge of only two densities and the molecular structure. These densities are

connected to the molecular nuclear-nuclear repulsive, electron-nuclear attractive and electron-electron repulsive potential energies, V_{nn} , V_{en} and V_{ee} respectively as^{10, 12}

$$(2/\pi) \int_0^\infty dK (I_{\text{TOT}}^{\text{EL}} - I_{\text{TOT}}^{\text{XR}} - \sum_{n=1}^M Z_n^2) = 2 \sum_{n>m}^M \sum_{m=1}^M \langle Z_n Z_m / R_{nm} \rangle_{\text{vib}} \quad (8)$$

$$-2 \sum_{n=1}^M Z_n \left\langle \int dr \rho(\vec{r}) / |\vec{r}-\vec{R}_n| \right\rangle_{\text{vib}} = \bar{V}_{nn} + \bar{V}_{ne}$$

$$\text{and } (2/\pi) \int_0^\infty dK (I_{\text{TOT}}^{\text{XR}} - N) = \left\langle \int_0^\infty dr_{12} P(r_{12}) / r_{12} \right\rangle_{\text{vib}} = \bar{V}_{ee} \quad (9)$$

A fourth energy quantity which does not occur in the expression for the total electronic energy of the molecule is given as

$$(2/\pi) \int_0^\infty dK I_{\text{E}}^{\text{XR}} = \left\langle \int dr p(\vec{r}) \int dr' p(\vec{r}') / |\vec{r}-\vec{r}'| \right\rangle_{\text{vib}} = \bar{V}_c \quad (10)$$

which is the classical Coulomb repulsive potential energy between two charge distributions which is a self energy in this case since both distributions are the same. From the virial theorem we know that the total energy E, is given in terms of the average potential energy by¹²

$$E = [\bar{V}_{nn} + \bar{V}_{en} + \bar{V}_{ee}] / 2 \quad (11)$$

In other words scattered x-ray and electron intensities obtained over sufficiently wide angular (K) range can be used to obtain various parts of the potential energy. Usually one uses vibrational spectroscopic and molecular structure information from other sources to obtain \bar{V}_{nn} so that only \bar{V}_{en} , \bar{V}_{ee} and \bar{V}_c are investigated. If one introduces the spherically averaged momentum density $\rho(p)$ obtainable from Compton experiments (γ -ray, x-ray or electron) then one also has the total energy as¹⁴

$$E = -T = - \int_0^\infty dp p^2 \rho(p) [p^2/2m]. \quad (12)$$

As a general rule, although not in every case, the HF approximation does an excellent job of predicting $p(\vec{r})$ and a rather poor job with $P(r_{12})$. This means that experiments which mainly measure $P(r_{12})$ have the greatest sensitivity to correlation. Since $p(p)$ contains all the information about the energy that $p(\vec{r})$ plus $P(r_{12})$ do, we might expect that the observation of ground state correlation effects from $p(p)$ might be a more difficult task than from $P(r_{12})$ although easier than with $p(\vec{r})$. This is indeed the case and the investigation of $I_{\text{TOT}}^{\text{XR}}$, I_{I}^{XR} and I_{E}^{EL} currently offers the best opportunities to document correlation effects. We will focus our attention here on these experiments. Note, however that some Compton experiments¹⁵ and more recently, some binary (e,2e) experiments which measure individual orbital momentum densities have exhibited slight sensitivity to ground state correlation effects¹⁶.

A. X-Ray Scattering

The use of x-rays to measure charge densities has a long history. The first modern measurements capable of

detecting electron correlation effects were carried out by Craseman and co-workers on H_2 using synchrotron radiation¹⁷. More recently Iijima and collaborators have employed the background ionization continuum radiation between 15 and 40 keV produced by a rotating anode tungsten x-ray target¹⁸. The "white" light beam was collimated and passed through a gas target. Scattered x-rays at a selected scattering angle were energy analyzed by means of a pure Germanium detector used in the pulse height mode. The scattered intensity as a function of energy at a fixed angle can then be used to determine the total x-ray scattered intensity as a function of the momentum transfer. So far it has not proved possible to separate the total x-ray scattering into its separate elastic and inelastic components. In order to do so would require a single crystal monochromator with a resolving power of a few eV. The currently used solid state detectors have resolutions on the order of 150 eV.

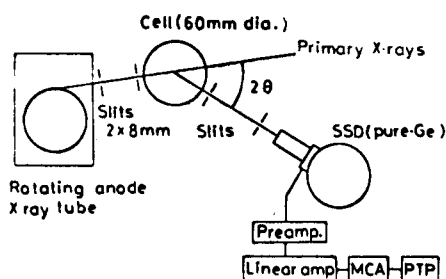


Fig. 1 - Schematic diagram of the energy-dispersive diffractometer. The gall cell is placed on a goniometer with a 2θ - scanning mechanism for the detector arm. Note that SSD stands for solid state detector. We wish to thank the authors of Ref. 19 for permission to reproduce their figure.

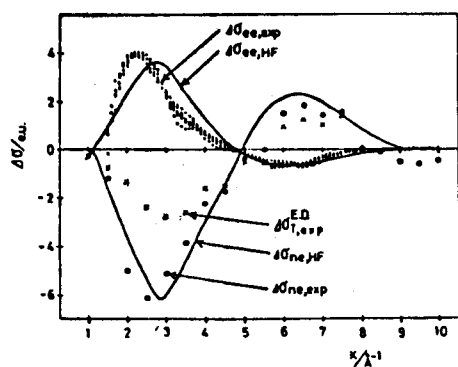


Fig. 2 - Comparison of the experimental $\Delta\sigma_{ee}$ with theoretical prediction based on a molecular HF wave function. Also shown are experimental $\Delta\sigma_{ne}$ (...) obtained from $\Delta\sigma_{ee}$ combined with $\Delta\sigma_{EL_T}$ (xxxxx) as compared with the HF theoretical values. We wish to thank the authors of Ref. 19 for permission to reproduce their figures.

A schematic of the apparatus used by the Gakushuin University group¹⁸ is shown in Fig. 1. In Fig. 2 their results for the molecule CO_2 are shown and compared to molecu-

lar HF values¹⁹. The symbols $\Delta\sigma_{ee,exp}$ and $\Delta\sigma_{ee,HF}$ are defined as the differences between the molecular result and the independent atom model (IAM) results¹². Such comparisons evolved historically from the fact that few theoretical molecular HF results were available and the IAM model was the only one at hand for comparison purposes. It is likely that the use of the IAM model will gradually be replaced by the use of molecular HF results for determining correlation effects. The interpretation $\Delta\sigma$ curves based on an IAM model is complicated by the fact that if one is discussing bonding or correlation effects it is necessary to understand to what extent the IAM model may itself represent part of these effects. A better approach which is becoming more feasible is to define $\Delta\sigma$ curves as the difference between the experiment and molecular HF theory if one wishes to discuss correlation and the difference between the experiment and the sum of all the atomic contributions in the molecule based on exact calculation (including correlation) for spherically averaged ground state atoms if one wishes to discuss bonding effects²⁰. These definitions are rigorous and provide a direct display of the sought for effect without the added complication of having to understand the idiosyncracies of the IAM model. In the case of CO_2 , although the authors used a comparison based on the IAM model, it is possible from the difference in $\Delta\sigma_{ee,exp}$ and $\Delta\sigma_{ee,HF}$ curves to see what the correlation to V_{ee} is doing. Note that it is positive for $K < 2.5 \text{ \AA}^{-1}$ and negative for $2.5 < K < 4 \text{ \AA}^{-1}$ with little contribution beyond. This means that correlation is increasing the electron-electron repulsive energy in the outer most part of the valence shell of the molecule and decreasing it in the inner regions. We can make such general statements because small momentum transfer corresponds to large impact parameters and vice versa. It is this extra degree of freedom provided by the scattering experiment, the momentum transfer dependence, that makes the scattering approach such a useful and important tool for investigating binding and correlation effects.

What does the future hold for x-ray measurements? Hopefully monochromator technology will be improved to the point where the separation of the elastic and inelastic scattering will become possible²¹. This goal may be further helped by the advent of new synchrotron light sources with peak energies in the x-ray range. Although the total scattered x-ray intensity is the easiest to measure there are certain technical difficulties in interpreting the results. This comes about because the inelastic scattering has certain kinematic factors due to conservation of total flux that depend on the energy loss²². Integrating over all energy losses to obtain the total scattering with the kinematic energy loss weighting leads to certain corrections in Eq. 2. This problem can be circumvented if energy resolved spectra are obtained. One major advantage of the x-ray total intensity measurement over the alternative electron scattering experiments is to be discussed in the next section of this paper and the other x-ray measurements is that the electron pair correlation function is obtained directly and is this recoverable in a unique way by taking the inverse Fourier transform.

B. Electron Scattering

The first experiments with sufficient sensitivity to observe correlation effects were carried out by Fink and

CHARGE DEFORMATION MAPS

Bonham²³ on atomic neon by measurement of the total scattered intensity. The first experiments measuring the effect of correlation on the elastic and total inelastic scattering separately were due to Wellenstein et al^{24,25} and were carried out on He and H₂. Duguet et al²⁶ have reported results for the elastic and inelastic scattering of Ne and these have been improved upon by McClelland and Fink²⁷. Recently Ketkar and one of the authors have published results for elastic scattering from He and inelastic scattering from He and N₂²⁸ and Fink and co-workers have carried out studies of the small angle elastic scattering for He, Ne, Ar, CO₂, N₂ and CH₄²⁹. The elastic cross section for H₂O has been reported by Shibata et al³⁰.

Just as in the x-ray case, there are certain technical difficulties in trying to interpret total scattering experiments³¹. However it is a much simpler problem to build energy analyzers with sufficient resolution (1-2 eV) to separate the elastic and inelastic scattering for the electron case and most laboratories working in this field now have this capability³². Hence we shall focus our attention here on the newer elastic and inelastic measurements.

For elastic scattering the difference between the experiment and the molecular HF description of the target molecules scattering, the correlation $\Delta\sigma$ function, has turned out to be a very difficult quantity to measure²⁷. In general, because the elastic scattering only depends on a knowledge of the one electron density, the correlation effects are very small. Several problems which must be dealt with are that intra molecular multiple scattering, a breakdown of the first born approximation, must be corrected for. This does not turn out to be a serious problem for inelastic scattering. For elastic scattering, if the atoms in the molecule belong to the first row in the periodic table, the corrections are manageable³¹. A second problem is the normalization of the data to place it on an absolute scale. This may be done by observing the scattering over a large range of momentum transfer (scattering angle) and then scaling the data to HF or IAM theory³¹. Because large angle scattering corresponds to small impact parameter collisions it is largely insensitive to binding and correlation effects. A validity check on this procedure can be obtained by comparison of the very small angle absolute intensities with bulk magnetic susceptibility measurements as explained in the following section. A second normalization procedure employs sum rule normalization of the inelastic spectrum and since the elastic scattering is obtained on the same scale this also normalizes it at the same time³³.

In Fig. 3 we show the recent results obtained by McClelland and Fink for atomic Ne²⁷. This work resulted from a controversy over whether or not the correlation correction to \bar{V}_{en} was negative as suggested by the earlier experimental work of Duguet²⁶ and the Bethe-Goldstone theory³⁴ or whether it was positive as suggested by CI calculations³⁵ and fits of experimental ionization potentials³⁶.

In Fig. 3 the correlation correction determined by a very careful study²⁷ clearly shows a positive contribution to the coherent x-ray scattering factor and hence suggests that the CI theoretical results are more reliable. It appeared that the results of Duguet et al²⁶ were due to normalizing their data at too small a value of the momen-

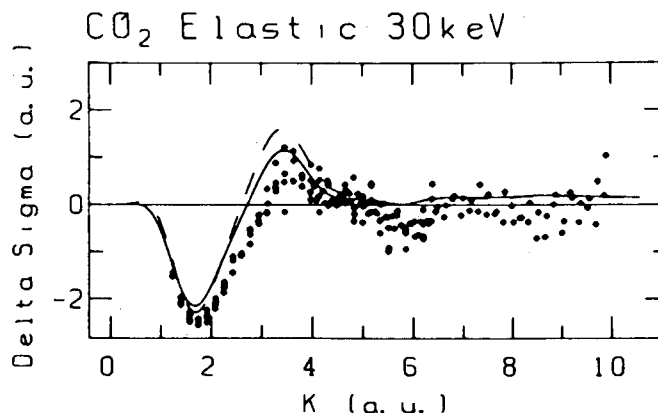


Fig. 3 - Neon ΔF_x curve showing the correlation effect on the one electron density. $\Delta F_x(K) = F(K) - F_{HF}(K)$ where $F(K)$ is the coherent X-ray scattering factor. We wish to thank the authors of Ref. 27 for permission to reproduce their figure.

tum transfer since McClelland and Fink²⁷ showed that when they used the Duguet et al normalization point they obtained agreement with their results. Very little is known about the effect of correlation on the one electron density except in the simplest systems and this is still an active area of research for both experiment and theory.

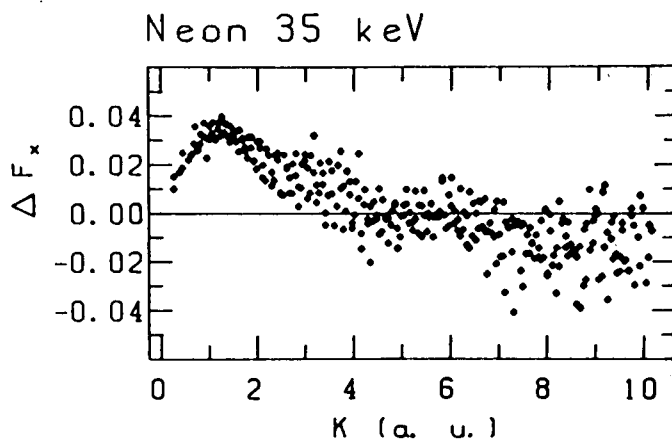


Fig. 4 - Difference cross sections of CO₂: experiment; HF Theory (-----) and correlated theory (.....).

In Fig. 4 the elastic results for CO₂ obtained by Fink et al²⁹ are compared with HF and CI theory. Note the very small difference due to correlation and the fact that the CI theory does agree better with experiment since the deviation is positive. In Fig. 5 the results from Fink et al²⁹ for N₂ are shown. Again, correlation improves agreement with experiment but this time a discrepancy exists in the region of the minimum at $K=4\text{\AA}^{-1}$. Finally these same workers have reported values for the elastic cross

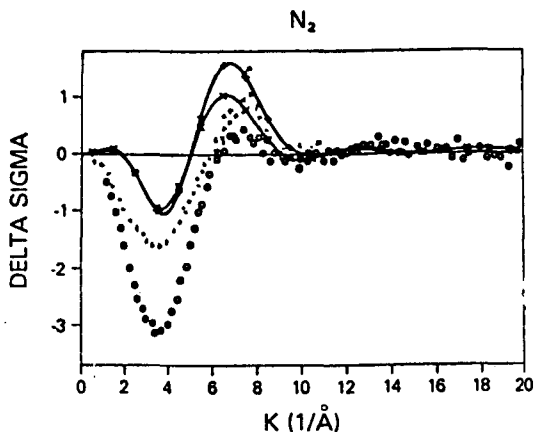


Fig. 5 - Difference cross sections of N_2 : (+++++) elastic data; (00000) total data, (---+---+---) HF elastic results and; (---x---x) correlated results.

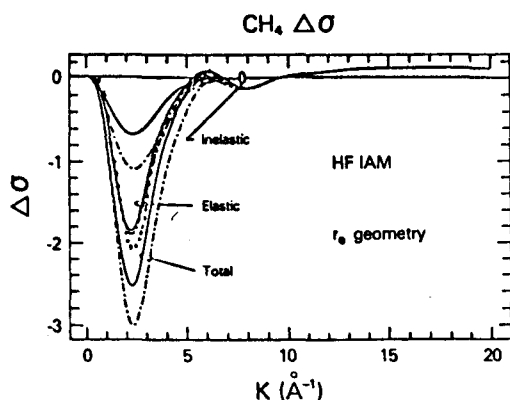


Fig. 6 - Difference cross sections of CH_4 : (+++++) elastic data; (----) HF theoretical results for elastic (middle) inelastic (top) and total (bottom); and (---.---) correlated (50%) results for elastic (middle); inelastic (top) and total (bottom).

section for CH_4 ²⁹ shown in Fig. 6. The agreement between theory and experiment is much better for this case. Shibata et al also found³⁰ close agreement between theory and experiment for H_2O .

While electron correlation does not in general strongly influence elastic scattering, its study is still of interest for several other reasons. Fink et al have discussed the feasibility of obtaining 3-D molecular one electron maps from gas phase electron scattering data²⁹. With the newer data this may prove to be an interesting possibility. In addition, certain moments of the charge density may be obtained from small angle elastic scattering as explained in the next section.

Let us now turn to measurements of inelastic scattering. In the first Born approximation the observed cross section σ differential with the respect to the energy loss (to the target) E and solid angle of detection Ω can be written as³⁷

$$(d^2 \sigma / dE d\Omega) = 4k(E) (df(K,E)/dE) / kK^2 E \quad (13)$$

where k is the electron incident momentum, $k(E) = (k^2 - E)^{1/2}$ is the final (scattered electron) momentum, $K^2 = k^2 + k(E)^2 - 2kk(E) \cos \theta$ is the momentum transferred by the incident electron which scatters through the angle θ with energy transfer E and df/dE is called the continuum generalized oscillator strength (GOS) defined as

$$(df(K,E)/dE) = E \sum_{\ell} | \langle \Psi_0 | \sum_{i=1}^N \exp(i\vec{K} \cdot \vec{r}_i) | \Psi_{\ell} \rangle |^2$$

$$\delta(E_{\ell} - E) / K^2 \quad (14)$$

where Ψ_0 is the initial electronic wave function of the target containing N electrons located at the points \vec{r}_i with respect to the center of mass principal axis coordinate system of the molecule and Ψ_{ℓ} is the wave function for the final state of the target after electron impact excitation. The Dirac delta function limits the possible excitations to those for which energy is conserved (accessible by an energy transfer of E). A similar expression can be written for bound state excitation³⁷. The importance of using the GOS formalism lies in the fact that certain energy loss moments of it result in expressions which only depend on ground state expectation values. The most useful of these for our purposes are³⁸

$$\int_{E_1}^{\infty} dE (df(K,E)/dE) = N + e \quad (15)$$

$$\int_{E_1}^{\infty} dE (df(K,E)/dE) / E = S(K) + s \quad (16)$$

where E_1 is the first energy loss and e and s are small corrections which are normally neglected and arise from rotational and vibrational excitation of the ground state. Two additional technical problems arise here: The integrations over the continuum GOS and sum over the bound state GOS (implicit in Eq. 15 and 16) assume that K is a constant independent of E and that the experimental data extend to infinite energy loss. Both of these problems have been extensively investigated and methods have been developed to obtain the necessary small corrections to employ the sum rules in an accurate fashion³⁹. Eq. 15 is used to place relative experimental data on an absolute scale which can then be used in Eq. 16 to obtain absolute values of the X-ray incoherent scattering factor. In fig. 7 the results for $\Delta S(K) = S(K)_{\text{expt}} - S(K)_{\text{HF}}$ for N_2 are displayed using 25 keV incident electrons. The crosses are from the work of Ketkar and Bonham⁴⁰ and the open circles are due to Barbieri and Bonham⁴¹. The solid line is a theory which accounts for more than 50% of the correlation energy. The dotted curve is a scaled version of the theory curve assuming that the missing correlation contributes to total with the same momentum transfer dependence as the calculated curve⁴². Our experiments suggests this assumption is incorrect. This appears reasonable on physical grounds since most of the missing correlation is associated with inner shell electrons which should yield correlation contributions at higher values of the momentum transfer. Experiments are currently underway to attempt to see if this is indeed the case.

In addition to N_2 similar results for $S(K)$ have been obtained for He ⁴³ and H_2 ⁴⁴. Here theory and experiment are in excellent agreement.

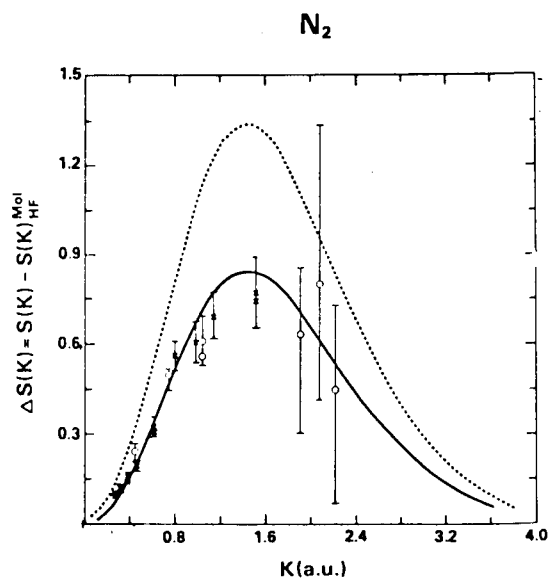


Fig. 7 - The $\Delta S(K)$ function for N_2 . Experiments points of Ketkar and Bonham*; Barbieri and Bonham Φ . The solid curve is CI theory and the dotted curve is scaled CI theory.

C. Small angle scattering and moments.

It is also possible to obtain information about ground state correlation by what we shall term indirect methods. For our purposes we shall take these to be various ground state expectation values such as the electronic moments (dipole, quadrupole, etc.). These moments can be obtained from several kinds of experiments but here we will focus on their connection to our scattering experiments. It is possible to expand any of our measured scattering cross sections in a power series in the square of the momentum transfer. The elastic cross section, for example, for a linear molecule with no dipole moment, can be written as⁴⁵

$$(d\sigma/d\Omega) = \gamma^2 a^2 (A + BK^2 + CK^4 + \dots) \quad (17)$$

where

$$A = [\langle R^2 \rangle^2 + 4Q^2/5]/9$$

$$B = [\langle R^4 \rangle \langle R^2 \rangle + 8 \langle R^2 Q \rangle Q/7]/90$$

$$C = [\langle R^4 \rangle^2 + 20 \langle R^6 \rangle \langle R^2 \rangle / 21 + 80 \langle R^2 Q \rangle^2 /$$

$$49 + 80 \langle R^4 Q \rangle Q/63 + 64\Phi^2 / 441] / 3600$$

where γ is a relativistic correction, a_0 is the Bohr radius and the capital letter R refers to total radial moments, Q to the total quadrupole moment and Φ to the total hexadecapole moment. Total means the difference between the nuclear and electronic contributions. Since one can usually obtain very accurate estimates of nuclear contributions from molecular structure information it is possible to obtain values for the outer electronic moments $\langle r^n \rangle$ ($n=2,4, \dots$) from electron scattering experiments. It is also possible to obtain estimates of $\langle r^2 \rangle$ from bulk suscep-

tibility measurements and molecular g factors⁴⁵. This means that bulk susceptibility data can be used to check the accuracy of the absolute scale in electron scattering experiments. The opposite is also possible. Recently theoretical estimates of $\langle r^2 \rangle$ for atomic neon were found to be in very serious disagreement with the bulk susceptibility result⁴⁶. Zhang and Fink⁴⁷ were able to derive a value for $\langle r^2 \rangle$ from their small angle elastic measurements of Ne. The HF value was 2.62 \AA^2 while the CI value was 2.673 \AA^2 . These were originally compared with the magnetic susceptibility result of 2.46 ± 0.05 . The electron scattering value of 2.69 ± 0.03 would thus seem to indicate the existence of some problem with the older magnetic measurement.

Fink and coworkers²⁹ have determined the coefficients A, B and C in Eq. 17 for N_2 ($58 \pm 1, -37 \pm 3, 7 \pm 3$) and CH_4 ($33 \pm 1, -25 \pm 2, 16 \pm 3$). As noted in the case of Ne above, the one electron electronic moments $\langle r^n \rangle$ are not particularly sensitive to electron correlation effects. One very significant aside needs to be mentioned. The electronic moments $\langle r^n \rangle$ for $n > 0$ probe the outer reaches of the charge distribution and are very sensitive to the tail behavior of the wave function which may have little to do with the quality of the total electronic energy given by the wave function for the system. It often turns out that HF molecular wave functions utilizing analytical orbital basis may give erroneous results for these moments because of incompleteness in the basis sets used⁴⁸. Several tests are available. If the numerical HF results which do not suffer from this problem are available then they should be preferred. If the HF wave function has been used to calculate the quadrupole or other electric moment then the values obtained can be compared with experiment. Usually the correlation effects are small and one should get reasonable agreement ($\sim 2\%$). Note that if a so called HF wave function gives a poor result for a given property compared to the HF numerical result due to insufficient orbital basis then no level of CI using such a basis will be able to achieve the correct answer.

Moments with greater sensitivity to correlation can be obtained by expanding the incoherent scattering factor, $S(K)$, in powers of K as⁴⁹

$$S(K) = K^2 [\langle r^2 \rangle + \langle \vec{r}_1 \cdot \vec{r}_2 \rangle] / 3 + K^4 [\langle r_{12}^4 \rangle - 2N \langle r^4 \rangle + 10 \langle r^2 \rangle^2 / 3 + 8Q_e^2 / 3] / 120 \quad (18)$$

where Q_e is the electronic contribution to the quadrupole moment. After Krause et al⁵⁰ who defined a correlation angle θ_c as

$$\cos \theta_c = \langle \vec{p}_1 \cdot \vec{p}_2 \rangle / T \quad (19)$$

where \vec{p}_1 and \vec{p}_2 are target electron momenta and T is the kinetic energy we may define a correlation angle as

$$\cos \theta_c = \langle \vec{r}_1 \cdot \vec{r}_2 \rangle / \langle r^2 \rangle \quad (20)$$

Note that $\langle \vec{r}_1 \cdot \vec{r}_2 \rangle$ is the quantity Ω_r in the notation of Inokuti et al⁵¹. For N_2 , using numerical Hartree Fock values, one obtains $\theta_c = 122^\circ$ and using experimental

values obtained from the work of Zeiss et al for⁵² $\langle r^2 \rangle + \langle r_1 r_2 \rangle$ and from magnetic susceptibility measurements⁴⁵ for $\langle r^2 \rangle$ one obtains $\theta = 129^\circ$ while using electron scattering data from Ref. 29 one obtains 128° . Hence one concludes that the correlation effect is on the order of 5% in $\cos \theta_c$ although it is larger in Ω_r . It is also tempting to think of the increase in angle as the additional self avoidance of electrons through angular correlation. Note that changes in radial averages such as $\langle r^2 \rangle$ due to correlation represent electron avoidance by radial or in-out correlation.

Very few results are yet available for moment values, however, the potential exists to obtain very interesting information from these sources. It appears feasible to obtain estimates to within a few percent for $\langle r^2 \rangle$, $\langle r^4 \rangle$ and possibly $\langle r^6 \rangle$ from small angle elastic scattering. Such studies combined with analysis of the small angle behavior of $S(K)$ should make it possible to obtain the moments $\langle r_{12}^2 \rangle$ and $\langle r_{12}^4 \rangle$. These moments can also be extracted from small angle total x-ray scattering or used to place total x-ray scattering measurements on an absolute scale. In principle one can also obtain correlation information on $\langle \vec{p}_1 \cdot \vec{p}_2 \rangle$ type moments from inelastic scattering experiments. This however involves the $S(1, K)$ sum rule which depends critically on accurate measurements of the high energy loss tail of the GOS which is experimentally very difficult³⁹.

SUMMARY

We have reviewed the current state of electron and x-ray scattering experiments and their ability to yield information sensitive to electron correlation effects in molecules. It is concluded that maximum sensitivity to correlation is obtained for experiments which are sensitive to the inelastic scattering and hence via sum rules to the x-ray incoherent scattering factors. The greatest sensitivity currently demonstrated has come from total x-ray and

inelastic electron scattering. Several experiments are now available where differences between experiment and HF molecular theory exceed the experimental uncertainty by more than an order of magnitude. For ground states no other experiments offer this sensitivity of the added dimension of the momentum transfer dependence. The latter allows one to infer qualitatively the radial region in the molecule where correlation effects are dominant and also the sign of their contribution to the correlation energy.

There are, of course, spectral transitions which are acutely sensitive to ground state correlation⁵³ but they also require an understanding of the excited state involved and are not direct measurements in the sense employed in this review.

Certain moments obtained from small angle expansions of the expressions for the scattered intensities also show sensitivity to correlation effects. Analysis of certain of these moments give qualitative insight into the global effect of angular correlation in the molecule.

It appears appropriate to us that this discussion of electron correlation should be part of an issue of *Química Nova* dedicated to the 60th birthday of Professor Ricardo Ferreira because of his long interest in the quantum theory of molecular structure. One of us (RAB) recalls long discussions over 20 years ago, on many of these same topics with Ricardo in Bloomington when he was a postdoctoral fellow in Professor Harrison Sull's research group in Quantum Chemistry.

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