

Compton Scattering and the Chemistry of Momentum Space

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Received August 4, 1972

The use of electromagnetic radiation to investigate the behavior of electrons in matter has played a major role in chemistry and physics in the twentieth century. Most of this effort has been devoted to determining where the electrons are, rather than how fast they are going. While this observation suggests numerous analogies to other areas of human endeavor, we shall limit the present discussion to a consideration of how one can measure the momenta of electrons in molecules and what such information can tell us about problems of interest to the chemist.

Until recently, momentum space has been almost exclusively the domain of the physicist, in particular of the solid-state physicist.^{1,2} However, a number of recent developments, both theoretical and experimental, suggest that excursions into this relatively uncharted region may prove rewarding for the venturesome chemist as well.

Two fundamental results of quantum mechanics are the Heisenberg uncertainty principle and the Dirac transformation theory. The former tells us that we cannot simultaneously measure the position and the momentum of an electron to arbitrary accuracy. The latter shows that the position and momentum representations are related to one another in such a way that, given a wave function in one representation, one can convert it to the other by taking a Fourier transform. These results suggest that (1) it will require a different type of experiment in order to obtain information about the electron's momentum, as opposed to its position; (2) only a single wave function calculation should be required to obtain both the position and the momentum distributions for a system; and (3) momentum space electron distributions should provide information about molecules different in nature from, but complementary to, the information obtained from position space distributions.

Professor Epstein's research interests include the chemistry of electron-deficient molecules, theoretical approaches to photochemistry, and Compton scattering and molecular momentum distributions. He received his A.B. from Harvard in 1966 and the Diploma in Advanced Mathematics from Oxford in 1967. He then returned to Harvard and took his Ph.D. in chemical physics. After a year as NATO Postdoctoral Fellow at Cambridge University, he joined the faculty of Brandeis University as Assistant Professor (in 1971).

Compton Scattering

The increase in the wavelength of electromagnetic radiation upon scattering by matter was first reported by Gray³ in 1920. Shortly thereafter, Compton⁴ explained both the angular dependence of the wavelength shift and the fact that the shift is independent of the scattering material. Compton's now familiar formulation of the scattering process in terms of the conservation of energy and linear momentum of a two-particle (photon and electron) system was derived independently by Debye.⁵ The theory, which considers the electron to be initially free and at rest, predicts a wavelength increase of $2h/mc \sin^2(\varphi/2)$, where φ is the angle of scattering. The quantity $h/mc = 0.02426 \text{ \AA}$ is known as the Compton wavelength.

Compton soon noted⁶ that the shifted line is broader than one would expect if the only source of broadening were the inhomogeneity of the scattering angle. Jauncey⁷ explained this additional structure by pointing out that electrons in molecules have nonzero momentum and that the magnitude of the Compton shift should depend upon the initial momentum of the scattering electron. It was not until 1929, however, that Dumond⁸ formulated a quantitative explanation of the shape (or profile) of the Compton line in terms of a Doppler shifting of the radiation due to the component of the electron's momentum along the scattering direction. A quantum mechanical derivation of Dumond's result has been given by Kilby.⁹

If we consider an isotropic medium in which the impulse approximation is valid (see below), then the

(1) The early work in this field is reviewed by J. W. M. Dumond, *Rev. Mod. Phys.*, **5** (1933).

(2) For an excellent recent review of Compton scattering and electron momentum distributions from the physicist's point of view see M. Cooper, *Advan. Phys.*, **20**, 453 (1971).

(3) J. A. Gray, *J. Franklin Inst.*, 633 (1920).

(4) A. H. Compton, *Bull. Nat. Res. Council. (U. S.)*, **20**, 19 (1922); *Phys. Rev.*, **21**, 483 (1923).

(5) P. P. Debye, *Phys. Z.*, **24**, 161 (1923).

(6) A. H. Compton, *Phys. Rev.*, **22**, 412 (1923).

(7) G. E. M. Jauncey, *Phys. Rev.*, **25**, 314, 723 (1925).

(8) J. W. M. Dumond, *Phys. Rev.*, **33**, 643 (1929).

(9) G. E. Kilby, *Proc. Phys. Soc., London*, **86**, 1037 (1965).

intensity of the Compton scattered radiation is given by^{8,9}

$$J(q) = \frac{1}{2} \int_{|q_1|}^{\infty} \frac{I(p) dp}{p} \quad (1)$$

The quantity $J(q)$ is known as the Compton profile, and the intensity of scattered radiation with "reduced wavelength" between q and $q + dq$ is proportional to $J(q)$. The parameter q gives the wavelength shift measured from the center of the Compton line and is essentially the electron's initial momentum along the scattering direction.

$$p_z = q \left(1 + \frac{h}{2mcl} + \frac{q}{mc} \right)^{-1} \approx q \quad (2)$$

The radial momentum distribution, $I(p)$, which appears in eq 1, is the square of the momentum wave function integrated over the momentum space angular variables. If we can measure the Compton profile, we can obtain $I(p)$ by differentiating eq 1.

$$I(p) = 2p \left| \frac{dJ(q)}{dq} \right|_{q=p} \quad (3)$$

The Impulse Approximation

Although the study of anisotropies in the momentum distributions of solids is a field of much current interest,² we will not discuss that question here, but will confine ourselves to studies of isotropic phases. One objection to the use of eq 1 and 3 in interpreting Compton scattering data is the possible failure of the so-called impulse approximation (IA), the assumption that the electron sees the same potential before and immediately after its interaction with the photon. An alternative statement of the IA is that the binding energy of the electron is negligible compared with the energy imparted to it by the photon, so that the final state of the electron may be adequately represented by a plane wave.

The energy transfer involved in a typical X-ray Compton scattering event is on the order of 1000 eV. For the lighter elements, lithium to neon, the 1s electrons have binding energies of hundreds of electron volts, while the valence electron ionization potentials are about an order of magnitude smaller. Thus, for all elements heavier than helium, the impulse approximation, at least for the more tightly bound electrons, is far from satisfactory.

How serious is the failure of the IA? Does it totally invalidate our simple interpretation of Compton scattering, or can some use still be made of a theory which rests upon the IA? At this point the complementarity of position and momentum space comes to our aid. For the light elements, the IA is valid for all but the 1s electrons. In position space, the 1s wave function is sharply peaked at the nucleus and then falls off quite rapidly; the more tightly bound the 1s electron, the more closely it is localized about the nucleus. The momentum space and position space wave functions are Fourier transforms of one another. If one transforms a function with a narrow peak in one space, one obtains a broad function in the

other space. For example, the Gaussian $\exp(-ar^2)$ transforms to the Gaussian $\exp(-p^2/4a)$ in momentum space; the widths are inversely proportional. Thus, even if the IA requires some modification for the inner-shell electrons, these electrons have a flat distribution in momentum space and hence make only a small, nearly constant, contribution to the Compton profile.

For detailed comparisons of theory and experiment, or for studies of heavier elements in which the IA may fail for more than just the K-shell electrons, more precise corrections to the IA are required.¹⁰ Bloch¹¹ showed that the Compton shift is overestimated in the IA by an amount proportional to the binding energy of the electron and inversely proportional to the square of the photon energy. By considering continuum final states instead of plane waves as in the IA, Eisenberger and Platzman¹² obtained qualitative agreement with Bloch's results and were able to calculate the exact Compton profile for a hydrogenic 1s electron. The difference from the profile predicted by the IA is small, but measurable with present techniques. A study¹³ of nitrogen, oxygen, and neon using two different X-ray wavelengths suggests that the Eisenberger-Platzman corrections to the IA give consistent and accurate results for K-shell electrons.

It is an interesting commentary upon the relationship between theory and experiment that, while the defect in the Compton shift was noted and studied¹⁴ at the time of Bloch's work, there is no mention of this phenomenon in the recent literature until the new theoretical study of the subject.¹² We note, however, that our own work¹⁵ and the one published paper¹⁶ which contains sufficient data to reveal the shift defect both show definite evidence that the peak in the Compton profile does occur at a shorter wavelength than predicted by the simple IA.

One obvious way to eliminate corrections due to electronic binding energies is to conduct the Compton scattering experiments with photons of high enough energy so that the IA is valid. In the following section, we discuss a recently developed technique which makes such experiments possible.

Experimental Determination of Compton Profiles

A variety of experimental techniques may yield information about the momentum distributions of electrons in molecules. A momentum distribution may be obtained from an analysis of the energy distribution of electrons inelastically scattered by a sample.¹⁷ However, accurate interpretation of such experiments is made extremely difficult¹⁸ by the rel-

(10) R. Currat, P. D. DeCicco, and R. J. Weiss, *Phys. Rev. B*, **4**, 4256 (1971), have calculated IA corrections for the L-shell electrons in aluminum.

(11) F. Bloch, *Phys. Rev.*, **46**, 674 (1934).

(12) P. Eisenberger and P. M. Platzman, *Phys. Rev. A*, **2**, 415 (1970).

(13) P. Eisenberger, *Phys. Rev., Part A*, **5**, 628 (1972).

(14) P. A. Ross and P. Kirkpatrick, *Phys. Rev.*, **46**, 223, 668 (1934); J. W. M. Dumond and H. A. Kirkpatrick, *Phys. Rev.*, **52**, 419 (1937).

(15) I. R. Epstein, B. G. Williams, and M. J. Cooper, *J. Chem. Phys.*, in press.

(16) R. J. Weiss, *J. Chem. Phys.*, **52**, 2237 (1970). Eisenberger¹³ does not appear to have found such a defect, but his only published raw data are graphical, making it difficult to draw any definite conclusions.

(17) A. L. Hughes and M. M. Mann, *J. Chem. Phys.*, **53**, 50 (1938); A. L. Hughes and M. A. Starr, *J. Chem. Phys.*, **54**, 189 (1938).

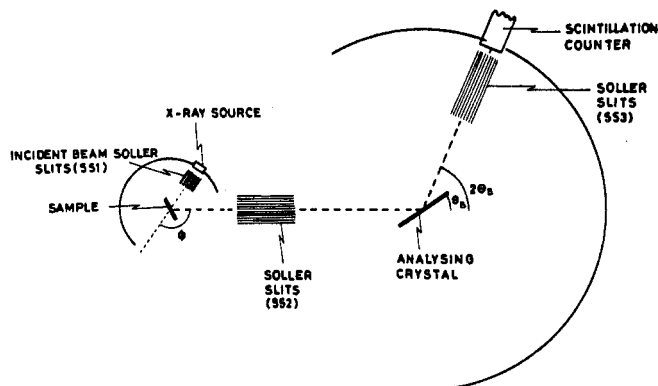


Figure 1. Experimental arrangement for X-ray Compton scattering (from M. J. Cooper, *Advan. Phys.*, 20, 453 (1971); reprinted by courtesy of *Advances in Physics*).

atively low incident energies available (failure of the IA) and by multiple scattering effects. The angular correlation between photons produced when thermal positrons annihilate with electrons in matter is determined by the initial momentum distribution of the electrons.¹⁹ Although positron annihilation experiments offer great promise for providing chemically useful information,²⁰ the need to have accurate positron wave functions makes it quite difficult to obtain reliable momentum distributions from angular correlation measurements at the present time.

The procedure used to obtain momentum distributions from Compton profiles has been outlined above. Until recently, nearly all Compton profiles were measured using either molybdenum (17.4 keV, λ 0.71 Å) or silver (22.2 keV, λ 0.56 Å) $K\alpha$ X-rays. The apparatus generally consists^{21,22} of an X-ray tube from which radiation passes through a set of Soller slits and impinges upon the sample. The radiation scattered through some fixed angle φ is again collimated and is wavelength analyzed with a lithium fluoride crystal and a scintillation counter. A typical experimental arrangement is shown in Figure 1. The wavelength of the scattered radiation is determined by the position of the counter *via* the Bragg equation. The count rate is measured at one position and then the detector is moved by a stepping motor. Thus the profile is built up point by point. The observed spectrum typically consists of a sharp doublet due to the elastic (thermal diffuse) scattering of the $K\alpha_1, K\alpha_2$ X-ray line, the broader Compton line at longer wavelength, and a flat background due to the Bremsstrahlung continuum. Such a spectrum is illustrated in Figure 2.

Once the spectrum has been measured, a number of steps must be carried out in order to obtain the Compton profile or the momentum distribution. These are: (1) wavelength-dependent corrections for absorption, relativistic, polarization, and detector efficiency effects; (2) corrections for the divergence of

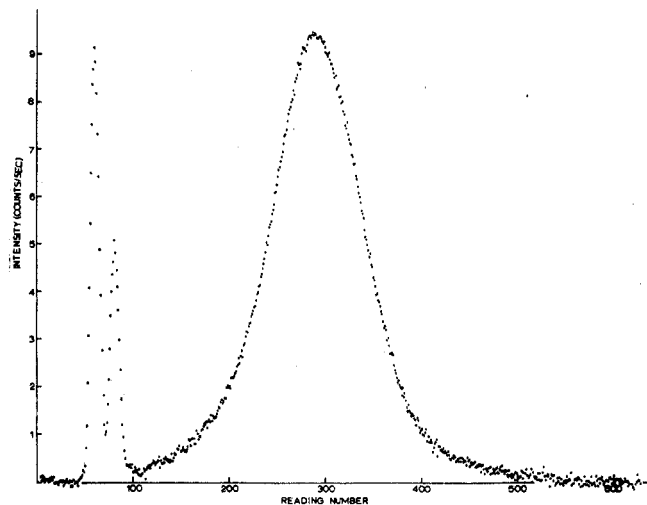


Figure 2. Raw data for Mo $K\alpha$ X-rays scattered by dioxane (I. R. Epstein, B. G. Williams, and M. J. Cooper, *J. Chem. Phys.*, in press; reprinted by courtesy of *The Journal of Chemical Physics*).

the incident beam; (3) deconvolution of the data to allow for the finite width of the apparatus function, and separation of the α_1 - α_2 components; (4) subtraction of the background; and (5) conversion from an X-ray wavelength to an electron momentum scale and normalization of the $J(q)$ curve. Steps 1, 2, and 5 are relatively straightforward and are discussed by a number of authors.² Several methods have been suggested to carry out the deconvolution^{23,24} and separation^{1,25} processes. Cheng, *et al.*,²⁶ have discussed the relation among the various deconvolution techniques and have derived expressions for the errors generated in the data processing.

A recent technique^{27,28} involving the use of high-energy γ rays in conjunction with a solid-state detector offers promise of minimizing or eliminating many of the difficulties inherent in X-ray Compton scattering. In γ -ray Compton-scattering experiments, the X-ray tube is replaced by a γ -ray source, such as ^{123m}Te (159 keV) or ^{241}Am (60 keV). The detection system consists of a lithium-drifted germanium [Ge(Li)] detector in conjunction with a multichannel analyzer, which measures all points in the Compton profile simultaneously, instead of sequentially as in the X-ray method.

The advantages of the γ -ray source are many. Obviously, the higher energy of the photons means that the IA will be satisfied even for relatively heavy elements. With a ^{123m}Te source, the energy transfer is so large (62 keV) that IA corrections are under 1% throughout the periodic table. A second advantage of using higher energy photons is that the cross section for absorption by the heavier elements is lower than for X-rays. In 3 days Eisenberger and Reed²⁸ were able to collect data on krypton using γ rays which

(18) W. E. Duncanson and C. A. Coulson, *Proc. Cambridge Phil. Soc.*, 37, 406 (1941).

(19) S. De Benedetti, C. E. Cowan, W. R. Konneker, and H. Primakoff, *Phys. Rev.*, 77, 205 (1950).

(20) For reviews, see "Positron Annihilation," A. T. Stewart and L. O. Roellig, Ed., Academic Press, New York, N. Y., 1967; J. H. Green and J. Lee, "Positronium Chemistry," Academic Press, New York, N. Y., 1964.

(21) M. J. Cooper and J. A. Leake, *Phil. Mag.*, 15, 1201 (1967).

(22) W. C. Phillips and R. J. Weiss, *Phys. Rev.*, 171, 790 (1968).

(23) J. S. Rollett and L. A. Higgs, *Proc. Phys. Soc., London*, 79, 87 (1962).

(24) D. Louer, D. Weigel, and R. Loubotin, *Acta Crystallogr., Sect. A*, 25, 335 (1969).

(25) W. A. Rachinger, *J. Sci. Instr.*, 25, 254 (1948).

(26) R. Cheng, B. G. Williams, and M. J. Cooper, *Phil. Mag.*, 23, 115 (1971).

(27) T. Fukamachi, S. Hosoya, Y. Hosokawa, and H. Hirata, *Phys. Status Solidi A*, 10, 437 (1972).

(28) P. Eisenberger and W. A. Reed, *Phys. Rev. A*, 5, 2085 (1972).

would have required over a year to obtain with conventional X-ray sources.

In addition to offering higher energies, γ -ray sources provide nearly monochromatic radiation with a low, easily measured background. Thus the step of separating the X-ray doublet is eliminated, while the errors involved in the deconvolution and background subtraction processes are greatly reduced. Also, the ability to measure a complete profile at once, instead of point by point, reduces the time necessary to complete an experiment, and hence minimizes the effects of instrumental instability. One possible drawback of γ -ray Compton scattering is the presence of sizable relativistic effects. However, it appears that the relativistic corrections can be made quite accurately.²⁸

Another possible source which would provide a continuous choice of photon wavelengths from X-rays to soft γ rays is the radiation produced by electron synchrotrons. The feasibility of synchrotron Compton scattering is currently under investigation.

Calculation of Compton Profiles and Momentum Distributions

There are two fundamentally different approaches to the calculation of momentum space wave functions. One can tackle the problem directly, by attempting to solve the quantum mechanical equations in the momentum representation. The alternative method is to calculate the wave function first in position space, and then to transform it to momentum space.

The direct approach has met with surprisingly little success. Apart from some formal theory²⁹ and work on problems in nuclear physics,³⁰ the only calculations carried out directly in momentum space have been those of McWeeny and Coulson on the helium atom³¹ and the hydrogen molecule ion.³² The major stumbling block in momentum space is the same one that must be overcome in position space—the difficulty of handling the interelectronic interaction terms. The situation is further complicated by the fact that the equations in momentum space are integral rather than differential equations. Nonetheless, in view of recent advances in computational techniques, it appears that a renewed attack upon the problem of calculating wave functions directly in momentum space may be justified.

The indirect or transform approach to momentum wave functions has been far more widely applied and considerably more successful. With the vast array of methods for computing wave functions in position space, there has been no shortage of material available for transformation. Given a wave function in position space, the Dirac transformation to momentum space is given by

$$\chi(p_1, \dots, p_n) = h^{3n/2} \int \prod_{i=1}^n [\exp(-ip_i r_i)] \Psi(r_1, r_2, \dots, r_n) d^3r_1 \dots d^3r_n$$

(29) M. Lévy, *Proc. Phys. Soc., London, Sect. A*, **204**, 145 (1950).

(30) E. E. Salpeter, *Phys. Rev.*, **84**, 1226 (1951); E. E. Salpeter and J. S. Goldstein, *ibid.*, **90**, 983 (1953).

(31) R. McWeeny and C. A. Coulson, *Proc. Phys. Soc., London, Sect. A*, **62**, 509 (1949).

(32) R. McWeeny, *Proc. Phys. Soc., London, Sect. A*, **62**, 519 (1949).

This transformation has the extremely useful properties that it preserves the form of the wave function and is independent of the spin functions. For example, if $\Psi(r_1, r_2, \dots, r_n)$ is a single Slater determinant or a multiconfiguration sum of such terms, involving orbitals $\varphi_s(r)$, then the momentum wave function χ is obtained from Ψ by replacing $\varphi_s(r)$ by $\gamma_s(p)$ where

$$\gamma_s(p) = h^{3/2} \int \exp(-ip \cdot r) \varphi_s(r) d^3r$$

Combining these results with eq 1 and 3 gives a justification for the observed additivity of individual orbital Compton profiles.

As early as 1929, Podolsky and Pauling³³ calculated the momentum wave functions which correspond to the solutions to the hydrogen atom Schrödinger equation. A flurry of experimental activity in the 1930's brought with it a number of calculations of the Compton profiles of atoms. For the most part, these calculations were rather crude, although Hicks,³⁴ using Hylleraas-type variational wave functions, did achieve good agreement with the experimental profiles of He and H₂.¹⁴

The first systematic studies of molecular momentum wave functions were those of Coulson and Duncanson.^{18,35} Although limited by the lack of accurate molecular wave functions in position space, Coulson and Duncanson obtained a number of important qualitative results. In particular they found that improvement of the wave function gives broader momentum distributions and Compton profiles, that momentum distributions may be usefully analyzed in terms of independent, localized molecular orbitals, that increased p character in a hybrid orbital broadens the momentum distribution, and that electrons have a higher average momentum perpendicular to a bond than along the bond direction. These principles, discovered in studies of H₂⁺, H₂, and simple hydrocarbons using only the most elementary wave functions, have been repeatedly confirmed and stand today as a basis for the analysis of calculations involving ever more sophisticated techniques.

Introduction of the self-consistent field (SCF) approach³⁶ as a practical means for computing wave functions has made possible the accurate prediction of many molecular properties. Roux, *et al.*,³⁷ used single-center, pseudo-atomic SCF wave functions to calculate momentum distributions and Compton profiles for a series of atoms and hydrides. Weiss, Harvey, and Phillips³⁸ obtained a reference set of atomic Compton profiles from Clementi's Hartree-Fock wave functions.³⁹

The first momentum space calculations employing true molecular SCF wave functions were performed by Henneker and Cade⁴⁰ for the diatomic molecules

(33) B. Podolsky and L. Pauling, *Phys. Rev.*, **34**, 109 (1929).

(34) B. Hicks, *Phys. Rev.*, **52**, 436 (1937).

(35) (a) C. A. Coulson, *Proc. Camb. Phil. Soc.*, **37**, 55 (1941); (b) C. A. Coulson and W. E. Duncanson, *ibid.*, **37**, 67 (1941); (c) C. A. Coulson, *ibid.*, **37**, 74 (1941); (d) W. E. Duncanson, *ibid.*, **37**, 97 (1941); (e) C. A. Coulson and W. E. Duncanson, *ibid.*, **38**, 100 (1942).

(36) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(37) M. Roux, M. Cornille, B. Tsapline, M. Roualt, and C. Tavaud, *Acta Crystallogr.*, **22**, 634 (1967).

(38) R. J. Weiss, A. Harvey, and W. C. Phillips, *Phil. Mag.*, **17**, 241 (1968).

(39) E. Clementi, *IBM J. Res. Dev.*, **9**, 2 (1965).

(40) W. H. Henneker and P. E. Cade, *Chem. Phys. Lett.*, **2**, 8 (1968).

N_2 and LiF. These authors used wave functions of Hartree-Fock quality to calculate momentum distributions (though not Compton profiles) and contour maps of both the total and difference (molecule minus separated atoms) electron densities in momentum space. They found, in agreement with the more qualitative results of Coulson and Duncanson, that molecule formation lowers the electron density in the low momentum region and increases the probability of finding an electron with high momentum, particularly in a direction perpendicular to the internuclear axis. Henneker and Cade have carried out detailed investigations of the momentum distributions and Compton profiles of atoms and diatomic molecules.⁴¹ They find that for these systems Hartree-Fock accuracy in the position space wave function is required to assure good agreement with experiment and accurate characterization of the bonding contributions to the momentum distribution. In a recently published study,⁴² they show that Hartree-Fock wave functions with a small correction for the impulse approximation in the K shell give excellent agreement with X-ray Compton scattering data for Ne, N_2 , and O_2 .¹³ The inclusion of correlation effects in the Ne wave function gave only slight improvement. Similar results, *i.e.*, good agreement between experiment and Hartree-Fock calculation and a relatively minor effect due to electron correlation, were also obtained by Eisenberger in his study of helium.⁴³

SCF studies of molecules containing more than two atoms have been almost completely limited to minimum basis set (MBS) wave functions. Epstein⁴⁴ calculated the first momentum distributions and Compton profiles obtained from transforming polycentric SCF wave functions. He found good, though far from perfect, agreement between the MBS and the experimental Compton profiles for water. He also observed that the mean momentum for hydrides A_nH_m is roughly proportional to the atomic number of atom A. In a more extended series of calculations, Epstein and Lipscomb obtained molecular momentum distributions and Compton profiles for boron hydrides⁴⁵ and hydrocarbons.⁴⁶ These studies show that, in spite of the apparent need for Hartree-Fock accuracy in calculations on atoms and diatomic molecules,^{41,42} good agreement with experiment and useful information about chemical bonding can be obtained from MBS-SCF calculations on larger systems.⁴⁷ Figure 3 illustrates the vast improvement which the MBS calculation gives over the profiles calculated from Hartree-Fock atoms and from the crude Coulson-Duncanson-type molecular orbital functions. The discrepancy between the two experimental profiles in Figure 3 (both of which

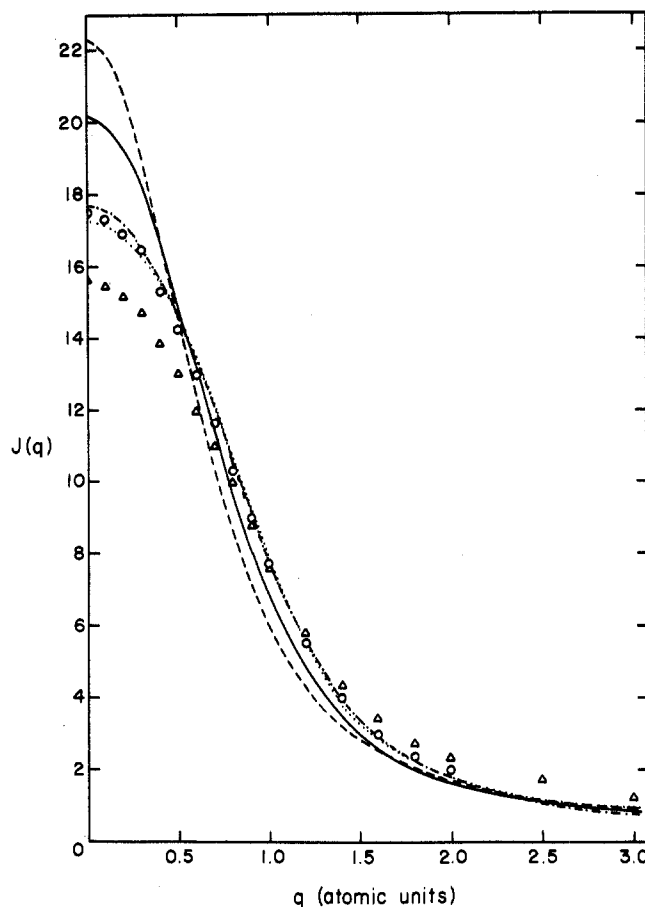


Figure 3. The Compton profile of benzene: O, experimental;²⁸ Δ , experimental;¹⁶ ---, Hartree-Fock atoms $6C + 6H$;³⁸ —, simple valence bond wave function;¹⁶ ..., LMO's;⁴⁶ - · - ·, minimum basis set SCF wave function.⁴⁶

claim better than 1% accuracy at the peak) also emphasizes the need for caution in comparing theory with experiment.

As one increases the size of the system under consideration, the effort involved in computing SCF wave functions, even at the MBS level of approximation, rapidly becomes prohibitive. Thus new approaches are required for calculations on large molecules. One of the most appealing of these approaches is the use of localized molecular orbitals⁴⁸ (LMO's). If one takes the molecular orbitals which result from an SCF calculation and subjects them to the unitary transformation which maximizes the sum of the intraorbital self-repulsion energies, one obtains a set of orbitals which leave the total wave function unchanged, but which may be interpreted as localized inner-shell, lone-pair, and bonding orbitals. Chemical intuition suggests that such orbitals should be to a large extent transferable. A C-H bond orbital in methane should look very much like a C-H bond orbital in decane. If such transferability holds, then one should be able to predict the properties of large molecules from the properties of their constituent LMO's, obtained from calculations on small molecules.

(41) W. H. Henneker and P. E. Cade, reported at Sagamore Conference III, Aussois, France, Sept 9-12, 1970.

(42) P. Eisenberger, W. H. Henneker, and P. E. Cade, *J. Chem. Phys.*, **56**, 1207 (1972).

(43) P. Eisenberger, *Phys. Rev. A*, **2**, 1678 (1970).

(44) I. R. Epstein, *J. Chem. Phys.*, **52**, 3838 (1970).

(45) I. R. Epstein and W. N. Lipscomb, *J. Chem. Phys.*, **53**, 4418 (1970).

(46) I. R. Epstein, *J. Chem. Phys.*, **53**, 4425 (1970).

(47) M. Roux and I. R. Epstein (*Chem. Phys. Lett.*, **18**, 18 (1973)) suggest that the virial theorem may provide a more useful criterion than the variational principle for determining the accuracy of quantities calculated from momentum wave functions.

(48) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963); *J. Chem. Phys.*, **43**, S97 (1965).

Strong evidence^{49,50} has been presented for the transferability of LMO's among hydrocarbons. Epstein⁴⁶ has calculated LMO momentum distributions and Compton profiles for all orbitals necessary to generate hydrocarbons and such homologous series as alcohols, esters, cyanides, and peptides. Thus Compton profiles may be estimated for even the largest of organic molecules. As shown in Figure 3, the LMO approach gives good agreement with experiment and with the full SCF calculation, even for a molecule as delocalized as benzene. The results of Inkinen, *et al.*,⁵¹ on hexane and decane show the accuracy of the LMO approach in predicting the Compton profiles of large molecules. One should perhaps note here that the utility of a set of prototype Compton profiles obtained from small molecules in the prediction of profiles for larger systems was suggested by Hicks⁵² over 30 years ago.

Experimental verification of the transferability of hydrocarbon LMO's in momentum space has recently been obtained by Eisenberger and Marra.⁵³ They employed a somewhat different set of orbitals (omitting inner shells and differentiating between single and double C-C bonds) than Epstein⁴⁶ and hence found rather different LMO profiles. However, their profiles for such molecules as cyclohexane and xylene are given to reasonable accuracy by *either* the LMO's obtained from their experiments on methane, ethane, and ethylene *or* by the rather different LMO's calculated for those molecules by Epstein. Even the somewhat disturbing prediction of the LMO theory that such dissimilar isomers as *n*-butyric acid and dioxane should have nearly identical Compton profiles has now been confirmed experimentally.¹⁵

The calculations discussed above all treat isolated rigid neutral molecules. Two preliminary studies have been made of the effects of molecular vibration on Compton profiles. Both of these investigations, one⁵⁴ on H₂ and the other⁵⁵ on H₂⁺, find that vibrational effects are on the order of 1% at low momentum and considerably smaller at high momentum. It is somewhat disturbing to note that the vibrational corrections result in narrower Compton profiles, thus increasing the discrepancy between theory and experiment.

Both theoretical and experimental profiles have been obtained for the ionic solids NH₄Cl,⁵⁶ NaF,⁵⁷ AlN,⁵⁸ BeO,⁵⁹ and MgO.⁶⁰ In all cases, the best agreement is found with wave functions representing the fully ionized species (*e.g.*, Al³⁺N³⁻). However,

the agreement is considerably inferior to that obtained for the covalent molecules discussed above, probably because of solid-state effects and overestimation of the ionic character.

Momentum Distributions and Chemical Bonding

In contrast to X-ray diffraction experiments, Compton scattering measurements are considerably more sensitive to valence electrons than to the more tightly bound inner shells. Coulson and Duncan^{35b} pointed to the study of electron momentum distributions as one of the most promising paths to identifying and understanding chemical bonds. The recent revival of theoretical and experimental interest in momentum distributions has brought new insights into the relation between electronic momentum and chemical bonding. Feinberg and Ruedenberg⁶¹ have analyzed the formation of the covalent bond in terms of the "paradoxical role" of the kinetic energy operator. These authors suggest that as two atoms approach one another, incipient bonding results not from a lowering of the potential energy (which actually increases slightly at large internuclear distances), but from a lowering of the component of kinetic energy (or momentum) along the internuclear axis. The ultimate decrease in potential energy and increase in kinetic energy in the molecule result in this view from the orbital contraction which occurs at the equilibrium distance. Whether or not one wishes to accept an analysis of bond formation based so heavily upon the variational principle and the competing forces of "kinetic energy pressure" and "nuclear suction," it is clear that the electron momentum is intimately related to the redistribution of charge which occurs when a bond is formed.

If bond formation puts more charge in the internuclear region, then the momentum (which is the gradient of wave function) must have a low value along the internuclear axis, since in the region of greatest electron density the wave function changes slowly in that direction. In the perpendicular direction the wave function falls off even more rapidly than in the isolated atom, due to the orbital contraction, and hence the momentum and kinetic energy in this direction must be larger. Antibonding systems should show large probabilities of high *p*, since the wave function must change quite rapidly if there is to be a node between the nuclei. In Figure 4 we show contour plots of the total and difference densities in momentum space for the strongly bound linear molecule acetylene. The relative increase in *p*_⊥ is evident, particularly in the difference map.

The success of the LMO approach in predicting Compton profiles suggests the validity of analyzing molecular momentum distributions in terms of individual bond orbitals. In this context small deviations from exact transferability of the LMO's may yield significant information about the nature of the chemical bond. An interesting example is provided by Table I, which gives the momentum expectation values, $\langle p \rangle$, for the C-H bond LMO's of several hydrocarbons. The width of the momentum distribution is seen to increase quite regularly with decrease

(49) S. Rothenberg, *J. Chem. Phys.*, **51**, 8, 3389 (1969).

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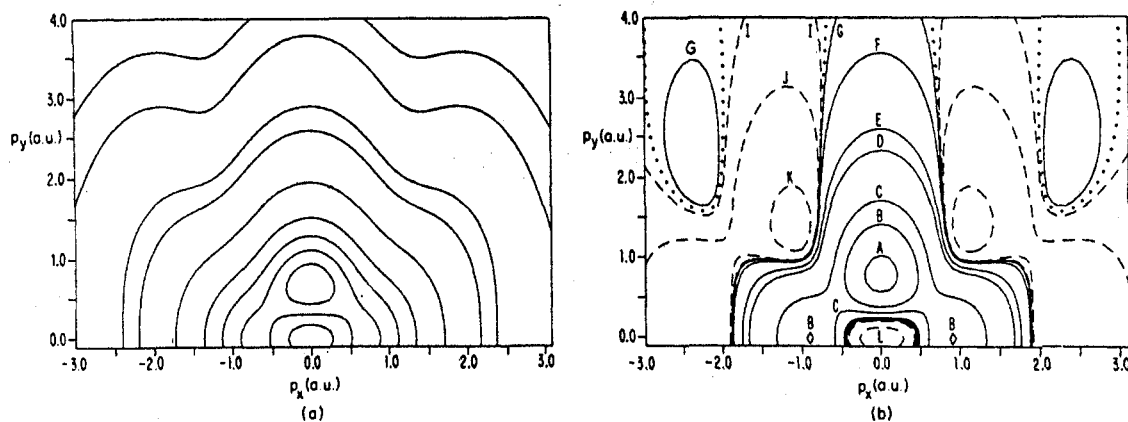


Figure 4. Momentum density in acetylene: (a) total density; (b) difference density (molecule minus noninteracting atoms) (from I. R. Epstein, *J. Chem. Phys.*, **53**, 4425 (1970); reprinted by courtesy of *The Journal of Chemical Physics*).

Table I
Momentum Expectation Values (Atomic Units) for
Hydrocarbon CH Bond LMO's^a

LMO	$\langle p \rangle$
HCCCH	1.091
HCCCH ₃	1.092
H ₂ CCHCHCHH'	1.113
H ₂ CCHCHCHH'	1.113
H ₂ CCH ₂	1.118
H ₂ CCHCHCH ₂	1.125
HCCCH ₃	1.131
CH ₄	1.132
H ₃ CCH ₃	1.133

^a Data from ref 46.

ing unsaturation of the carbon atom. The ordering triple bonded C < doubly bonded C < conjugated single-bonded C < hyperconjugated single-bonded C < single-bonded C is quite remarkable. An analysis of the momentum density of benzene⁴⁶ indicates that the σ - π separability approximation breaks down in momentum space to about the same degree as in position space.

One way in which Compton profile measurements and momentum distributions might provide information about bonding is through energy calculations. Given a complete radial momentum distribution $I(p)$, one can easily obtain the expectation value $\langle p^2 \rangle$ which gives the kinetic energy and, by the virial theorem, the total energy. In fact, Compton scattering may offer a viable alternative to traditional spectroscopic and thermodynamic techniques for such determinations. However, obtaining energies from Compton scattering data will require measurements at much higher values of q than are currently employed.

It can be shown⁶² that for $n \geq 0$

$$\langle p^n \rangle \equiv \int_0^\infty p^n I(p) dp = 2(n+1) \int_0^\infty q^n J(q) dq \quad (4)$$

where $I(p)$ is the radial momentum distribution and $J(q)$ is the Compton profile. In X-ray Compton scat-

tering experiments, q_{\max} , the maximum value of q at which $J(q)$ is measured, is limited by scattering from other orders of reflection of the analyzing crystal, while in γ -ray work q_{\max} is generally set to give accurate normalization of the profile. If we consider Slater-type atomic orbitals (with exponent ξ), we can obtain analytical expressions for $J(q)$. By direct integration, we find that, in order to achieve 1% accuracy in $\langle p^0 \rangle$, the normalization integral, we must have the ratio q_{\max}/ξ greater than or equal to 1.9 for 1s orbitals.⁶³ For hydrogen, this requires a q_{\max} of about 1.9 au; for sulfur, about 30 au, far beyond the practical limits of X-ray experiments and comparable to the most ambitious of the γ -ray experiments.²⁸ If we require 1% accuracy for the energy, i.e., for $\langle p^2 \rangle$, the situation is far less fortuitous. For 1s orbitals, the major contributors to the energy, we must have $q_{\max} \geq 6\xi$. While such a situation is possible in γ -ray experiments, it has not yet been attained for any systems that we are aware of.

The Future

From the experimentalist's point of view, the introduction of γ -ray Compton scattering promises to revolutionize the study of electronic momentum distributions. Instead of being limited to a few light elements, one may now explore the entire periodic table. For example, detailed studies of the anisotropies of the d-electron momentum distributions in transition metals⁶⁴ should now be possible. Experiments can be carried out in days instead of months, so that studies of sets of related systems are now feasible. Profiles can be measured over a much broader wavelength range, making possible the calculation of molecular energies as suggested above as well as the detailed study of the inner-shell electrons.

In view of its clear-cut advantages over X-ray techniques, it appears that γ -ray Compton scattering will soon become the dominant technique in the field. However, X-ray measurements do have the potential for higher resolution than γ rays, which are limited by the properties of the detector. Hence X-ray Compton scattering is likely to survive as a

(62) The derivation of eq 4 and a more detailed discussion of its use in interpreting Compton scattering data will be published elsewhere.

(63) The requirements are less stringent for higher principal quantum numbers. For example, 1% accuracy in $\langle p^0 \rangle$ for 2p orbitals (which have smaller exponents than 1s orbitals) requires $q_{\max}/\xi \geq 1.6$.

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high-resolution technique for the study of "fine structure" effects in the Compton profile and momentum distribution.

An exciting recent development in Compton scattering is the report⁶⁵ of a technique for separating the contributions of individual orbitals to the Compton profile. By measuring only photons which were Compton scattered in coincidence with the fluorescent K X-rays emitted by the scatter, Fukamachi and Hosoya were able to measure the profile of the 1s electrons in Fe, Ni, and Cu. If this coincidence technique can be perfected, it should yield information at least as useful as that available from ESCA experiments, particularly since Compton scattering provides a full orbital distribution while ESCA offers only one (or at most several) parameters for each orbital.

Compton scattering may prove to be useful in the study of solution processes. As yet, no Compton measurements have been undertaken on solutions, but recent positron annihilation work on metal-ammonia solutions⁶⁶ suggests that such studies may be quite revealing.

Nearly all the calculations discussed here were carried out by transforming position space wave functions which employed the independent-electron molecular orbital approximation. Although the results achieved with this method have been quite good, a systematic investigation of many-electron effects and the calculation of momentum distributions and Compton profiles from other types of wave functions are desirable. The use of natural orbitals offers a promising route toward both of these goals, and the studies of Benesch and Smith⁶⁷ on the lithium atom represent an important step in this direction.

As experimentalists turn their attention to larger systems, particularly polymers¹⁶ and molecules con-

taining heavy atoms, careful investigation of the LMO approximation and of other methods for dealing with large numbers of electrons becomes imperative. Statistical approaches to the calculation of electronic wave functions and momentum distributions seem quite attractive in this respect. The recent success of the SCF- $X\alpha$ method⁶⁸ in dealing with large systems merits a consideration of its use in momentum space calculations, while application of Thomas-Fermi theory⁶⁹ may offer a sort of bridge between the transform and direct methods of calculating momentum wave functions.

Compton scattering and electronic momentum distributions offer a vast amount of information about chemical systems. Unfortunately, most people, chemists not excepted, have their intuitions rather closely localized in position space. While the notion that "all Compton profiles look alike" (and are therefore uninteresting) is fading,⁷⁰ nearly all of us experience a feeling of disorientation if asked to think in terms of momentum rather than position. For example, a contour map of the momentum density of H_2 consists only of a single peak at the origin surrounded by descending elliptical contours. Without the nuclei to serve as familiar landmarks, we are, at least temporarily, left groping. It is in this area, in the development of chemical intuitions in momentum space, that we hope and expect to see the most significant advances in the coming years.

Much of this work was supported by a National Science Foundation Predoctoral Fellowship, a NATO Postdoctoral Fellowship, and a grant from the Petroleum Research Fund, administered by the American Chemical Society. I am indebted to many, many teachers, collaborators, and colleagues, especially C. A. Coulson, W. N. Lipscomb, R. J. Weiss, M. Cooper, and B. G. Williams, for encouragement and inspiration.

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