

## Reports from Other Journals

# Electron-Momentum Spectroscopy and the Measurement of Orbitals: Interesting Results for Chemists from the *American Journal of Physics*

by Frank Rioux

I would like to bring "Measuring Orbitals and Bonding in Atoms, Molecules, and Solids" by Vos and McCarthy (*J*) to the attention of the readers of the *Journal*. This article appeared in the June 1997 issue of the *American Journal of Physics* and deals with, as its title suggest, concepts of great interest to chemists. The abstract of this paper provides a good summary of the results reported:

The cloud of negative charge that determines the relative positions of the nuclei in a molecule or solid can be understood in terms of the motion of the electrons that form the cloud. Usually one pictures the charge cloud as a distribution in coordinate space. One can equally well picture it as a distribution of velocities, i.e., in momentum space. The probability that an electron has a certain energy-momentum combination is called the energy-momentum density. It is directly measured by electron-momentum spectroscopy. **The results of this technique provide the most direct experimental documentation of simple ideas of orbitals and bonding, thus opening a fresh and comprehensive perspective on electronic structure [emphasis added].** We show how measurement of the motion of electrons in solids can help us understand the bonding of atoms in molecules and solids. We [also] give examples of a free-electron metal and an ionic insulator.

Chemists generally seek solutions ( $\Psi(q)$  and  $E$ ) to Schrödinger's equation in coordinate space ( $q = x, y, z, r, \theta, \phi$ ; etc.). Quantum mechanical dogma teaches that  $\Psi(q)$  contains all of the physical information knowable about the system under study and the postulates of quantum theory consist of precise mathematical procedures for extracting the values of physical observables from  $\Psi(q)$ . In spite of the great success of quantum theory in explaining atomic and molecular phenomena,  $\Psi(q)$ , manifested as the probability density  $|\Psi(q)|^2$ , has eluded direct physical measurement.

However, Schrödinger's equation can also be formulated and solved in momentum space yielding  $\Phi(p)$ . The solutions to Schrödinger's equation in coordinate space and momentum space are formally equivalent and therefore contain the same information about the physical properties of the system under study. This formal equivalency is expressed by a Fourier transform, which allows one to generate  $\Phi(p)$  from  $\Psi(q)$ , or  $\Psi(q)$  from  $\Phi(p)$ .

$$\Phi(p) = (2\pi)^{-3/2} \int \exp(-ip \cdot r) \Psi(r) dr$$

$$\Psi(r) = (2\pi)^{-3/2} \int \Phi(p) \exp(ip \cdot r) dp$$

This is one of the reasons electron-momentum spectroscopy (EMS) experiments are so important. Vos and McCarthy show that under appropriate experimental conditions the momentum distribution  $|\Phi(p)|^2$  for an individual electronic state is directly measurable. Owing to loss of phase information one cannot, strictly speaking, use  $|\Phi(p)|^2$  to derive  $|\Psi(q)|^2$ . However, as indicated above, a theoretical  $\Psi(q)$  can be Fourier transformed to  $\Phi(p)$ , and this yields a theoretical  $|\Phi(p)|^2$  that can be compared with experiment. Because of the formal equivalence between  $\Psi(q)$  and  $\Phi(p)$ , this comparison with EMS data can be interpreted as a direct test of the validity of  $\Psi(q)$ . Thus, one of the important uses of EMS is to evaluate wave functions at various levels of theory for a variety of atomic and molecular systems.

The one-electron hydrogen atom offers a simple introduction to the method. In Figure 1  $|\Phi(p)|^2$  is calculated for the hydrogen ground state by the Fourier transform of the hydrogen 1s orbital using Mathcad and is then compared with EMS data. The conclusion is clear, the Fourier-transformed coordinate space wave function is in excellent agreement with the experimentally measured momentum distribution.

Obtaining similar orbital information from EMS for multi-electron systems offers significant challenges, and Vos and McCarthy outline the experimental conditions under which the orbital approximation for many-electron atoms and molecules is valid. Figure 2 compares EMS results for the 3s and 3p valence orbitals of argon with Fourier-transformed Hartree-Fock SCF wave functions.

At the introductory molecular level, Vos and McCarthy juxtapose theoretical and experimental results for  $H_2$  and the

### Momentum Distribution for Hydrogen 1s Orbital

The square of the absolute magnitude of the Fourier transform for the 1s orbital

$$|\Phi(p)|^2 = \left| \frac{1}{\sqrt{8\pi^4}} \left( \int_0^\infty \int_0^\pi \int_0^{2\pi} \exp(-r) \exp(-ipr \cos \theta) r^2 \sin \theta d\phi d\theta dr \right) \right|^2$$

yields  $|\Phi(p)|^2 = \frac{8}{\pi^2(1+p^2)^4}$

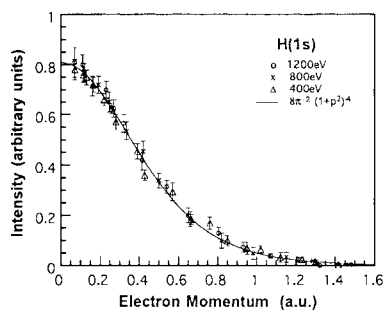


Figure 1. Comparison of theoretical and experimental momentum distribution functions for the hydrogen atom. Reprinted with permission from *Am. J. Phys.* **1997**, *54*, p 548; ©1997, American Association of Physics Teachers.

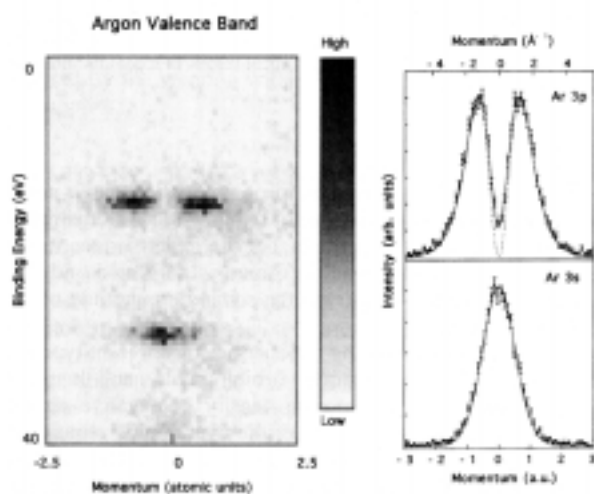


Figure 2. Comparison of theoretical and experimental momentum distribution functions for the argon 3s and 3p valence orbitals. Reprinted with permission from *Am. J. Phys.* **1997**, 54, p 548; ©1997, American Association of Physics Teachers.

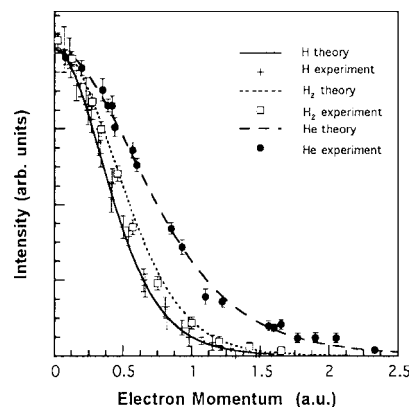


Figure 3. Comparison of theoretical and experimental momentum distribution functions for H, He, and H<sub>2</sub>. Reprinted with permission from *Am. J. Phys.* **1997**, 54, p 549; ©1997, American Association of Physics Teachers.

Fourier transform of the PIB coordinate-space wave function:

$$\Phi(p, n) = \frac{\int_0^1 \sqrt{2} \sin(n\pi x) \exp(-ipx) dx}{\sqrt{\pi (i^2 p^2 + n^2 \pi^2)}} \left( \exp(-ip) n\pi \cos(n\pi) + \exp(-ip) ip \sin(n\pi) - n\pi \right)$$

Plot the energy-momentum density on a two-dimensional grid.

$$N = 120 \quad j = 1 \dots N \quad k = 1 \dots 8 \quad p_j = -40 + \frac{j-2}{3} \quad n_k = k$$

$$\text{Energy-Momentum-Density}_{j,k^2} = \overline{\Phi(p_j, n_k)} \Phi(p_j, n_k)$$

The horizontal axis is the momentum,  $p$ , and the vertical axis is  $k^2$  and is therefore proportional to the energy of the state.

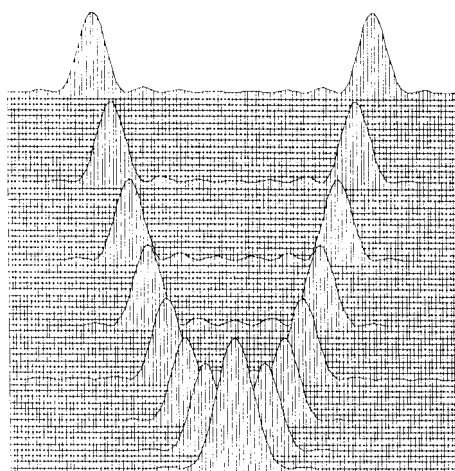
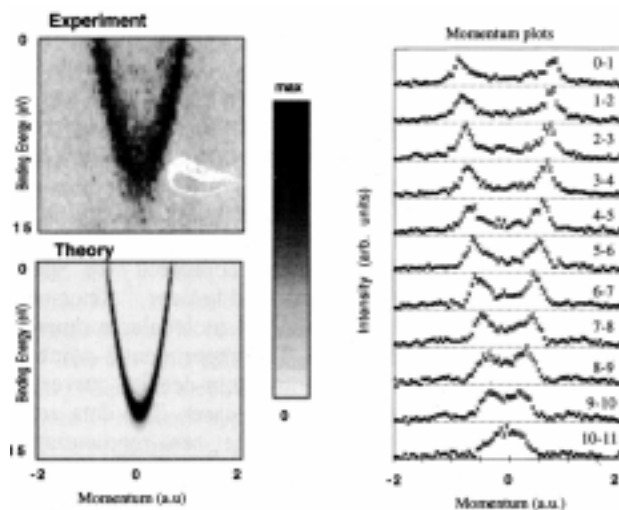


Figure 4. Energy-momentum distribution for the particle in the box derived from Fourier transform of the coordinate space wave function compared with experimental EMS data on aluminum thin films. Lower part reprinted with permission from *Am. J. Phys.* **1997**, 54, p 550; ©1997, American Association of Physics Teachers.



## Reports from Other Journals

continued from page 157

related atomic species H and He as shown in Figure 3. While the theoretical calculations were carried out at the Hartree–Fock SCF level, it is easy to show that even a simple scaled hydrogenic orbital

$$\Psi(r) = \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha r)$$

for He and a  $1\sigma_g$   $H_2$  molecular orbital constructed from such orbitals under the LCAO-MO approximation receives experimental support from the EMS experiments.

The treatment of metallic solids is based on EMS measurements on aluminum thin films. The simplest approach to metallic solids is to assume that their valence electrons are quantum mechanical particles in a box. Figure 4 calculates the momentum–space wave function by Fourier transform of the particle-in-a-box eigenfunctions and then displays the energy–momentum density. The favorable qualitative agreement between this figure and the EMS measurements, also shown in Figure 4, strongly suggests that this simple model captures the basic behavior of the valence electrons of metals. Of course, because of the macroscopic size of the sample (large box, closely spaced energy levels), the experimental energy–momentum distribution is continuous.

Finally the authors expose the aluminum thin film to air, creating an  $Al_2O_3$  coating on the surface. Conventional chemical wisdom suggests that aluminum oxide consists of discrete isoelectronic ions,  $Al^{3+}$  and  $O^{2-}$ , with electrons in 2s and 2p orbitals and limited opportunity for orbital overlap between ions: that is, no band formation. And, indeed, the EMS results for  $Al_2O_3$  bear little resemblance to those for the aluminum thin film, but look similar to the 3s and 3p atomic orbitals of argon, as Figure 5 clearly shows.

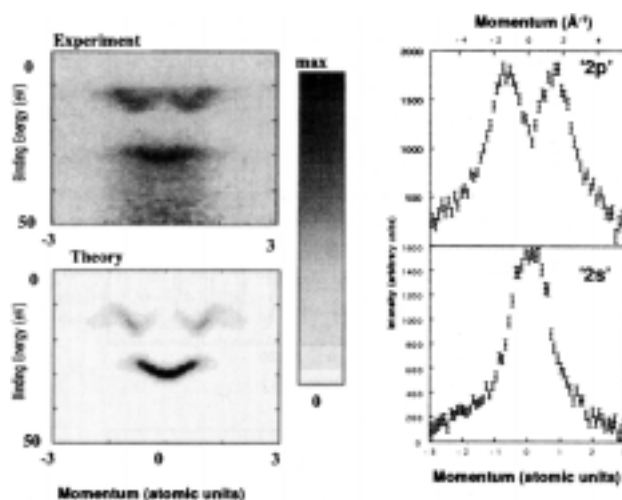


Figure 5. Electron-momentum spectroscopic data for  $Al_2O_3$ . Reprinted with permission from *Am. J. Phys.* **1997**, *54*, p 551; ©1997, American Association of Physics Teachers.

In summary, Vos and McCarthy describe important experimental and theoretical results about subjects of interest to chemists, based on a form of spectroscopy (EMS) that is not widely used by chemists.

## Literature Cited

1. Vos, M.; McCarthy, I. *Am. J. Phys.* **1997**, *65*, 544–553.

*Frank Rioux is in the Department of Chemistry, Saint John's University, College of Saint Benedict, Saint Joseph, MN 56374; email: frioux@csbsju.edu.*