Wave Functions Derived by Quantum Modeling of the Electron Density from Coherent X-Ray Diffraction: Beryllium Metal

L. Massa and M. Goldberg
Chemistry Department, Graduate School and Hunter College, City University of New York, New York, New York 10021
and
C. Frishberg[(a)]
Center for Advanced Studies, University of New Mexico, Albuquerque, New Mexico 87131
and
R. F. Boehme and S. J. La Placa
IBM T.J. Watson Research Center, Yorktown Heights, New York 10598

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A single-determinant experimental Be hybrid-atom wave function is obtained by the quantum formalism of Clinton and Massa, from Larsen and Hansen's single-crystal x-ray diffraction data. Physical properties calculable from this wave function are unobtainable from current methods of diffraction analysis. The least-squares fit using *all* experimental data gives an R factor of 0.0018, and quantitatively describes charge redistribution due to crystal bonding in agreement with *ab initio* calculations.

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This paper demonstrates that an approximate although quantum mechanically valid wave function can be obtained from experimental x-ray diffraction data. Such an experimental wave function allows the quantitative calculation of all physical properties, within the approximations incorporated in the wave function, by use of the usual rules of quantum mechanics. This includes, for example, properties such as the kinetic energy or Compton momentum profile, which are not obtainable from existing methods of diffraction analysis. Additionally, the wave function's orbital-basis contributions provide a quantitative deconvolution of the total crystal electron density into the fundamental components responsible for bonding. Indeed, the x-ray orthonormal orbital model of crystallography,[1] here applied to the case of beryllium,[2] demonstrates a powerful new potential in density analysis of x-ray scattering data.

The formalism of Ref. 1 can, in principle, be applied to yield orbitals and a Slater determinant characteristic of the full crystal. Here, however, we apply the formalism in a restricted sense, obtaining orbitals and a Slater determinant characteristic of D_{3h}-hybridized Be atom fragments, which, placed at their lattice positions, define the "exact" electron density of the Be crystal. This is a compromise of the crystal-field sort in that we attempt to represent the local fragments in the crystalline environment but give up any representation of the extended system that is Bloch–wave-vector dependent. Of course, those quantities determined solely by the density which is reproduced exactly, by construction, from fragment superposition, are calculable. The atomic hybrid model represents the next step in wave-function complexity beyond the spherical-atom ground-state wave function commonly used in x-ray diffraction analysis. The main features of our calculation, which results in the valence orbital and density matrix of Be, are as follows. The orbitals $\boldsymbol{\phi}$ of a Be hybrid-atomic fragment are obtained as a superposition of "atomic" basis functions $\boldsymbol{\psi}$. In this basis, the density matrix is $\rho(r,r') = 2\,\mathrm{Tr}\mathbf{P}\boldsymbol{\psi}(r)\boldsymbol{\psi}^{\dagger}(r')$. The population matrix $\mathbf{P}$ is treated as a set of experimental parameters chosen to fit the x-ray scattering factors as closely as possible, in a least-squares sense. In order to ensure N representability, i.e., that the orbitals $\boldsymbol{\phi}$ and the single determinant of those orbitals are recoverable from $\rho(r,r')$, it is imposed as a constraint that the population matrix be a normalized projector, i.e., $\mathbf{P}^2 = \mathbf{P}$ and $\mathrm{Tr}\mathbf{P} = N$. Any procedures equivalent to that described above constitute a quantum model of the crystallographic experiment.[1]

The form of the x-ray structure factor used in our calculation is just the ordinary expression for Be available from the *The International Tables of Crystallography*,[3] with the important difference that the standard spherical-atom scattering factor commonly used is here replaced with a more general scattering factor $2\,\mathrm{Tr}\mathbf{P}\mathbf{f}_{\mathrm{Be}}$, expressive of the quantum mechanical nature of the crystal electron distribution. The matrix $\mathbf{f}_{\mathrm{Be}}$ contains as elements Fourier transforms of basis products. The basis used has core and valence components. (The model discussed here for beryllium may be expected to also apply for larger systems. An increased number of core orbitals will not affect the method adversely, as these may be obtained from atomic Hartree-Fock calculations, so long as the core is not much affected by crystallization. With reference to increased numbers of valence orbitals, the formalism used here carries over in the same way so long as the number of data still exceeds the total number of model parameters. This will be true in many interesting systems as the number of x-ray data roughly scales

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with the size and number of atoms in the structure. We have examined this matter elsewhere in some detail.[4]) The core orbital is set equal to the Be free atom 1s core of Huzinaga[5] and is held fixed. The valence basis is obtained from a Be 2s orbital[5] and a single set of floating spherical Gaussian orbitals. These are Schmidt orthogonalized to the core and subsequently Löwdin orthonormalized. The net result is an efficient two-element basis for representation of the Be hybrid valence orbital, and the valence population matrix $\mathbf{P}$ is only of dimension 2×2. In the density, P_{11}, P_{22}, and P_{12} respectively weight the squared orthonormalized basis functions generated by the 2s orbital, the floating Gaussian orbitals, and the 2s-Gaussian cross terms. We obtain the "best" hybridized electronic structure in our representation by minimziation of the standard crystallographic least-squares functional.

The parameters, with respect to which the functional is full matrix least-squares minimized, have the following optimal magnitudes. [The experimental data contain errors which in the nature of least-squares procedures propagate into all the parameters of our model. In the text, quantitative estimates of parameter errors are shown in brackets after each optimal parameter value. In particular, errors are listed for elements of $\mathbf{P}$ defining the density matrix. Corresponding errors for the orbital wave functions $\boldsymbol{\phi}=\mathbf{C}\boldsymbol{\psi}$ follow from the factorization $\mathbf{P}=\mathbf{C}^{\dagger}\mathbf{C}$. Later, see also Fig. 3, which indicates that the errors in our model are random within the bounds of experimental error for the structure factors $F(k)$.] The population coefficient $P_{22}=0.355(40)$, together with normalization, Hermiticity, and idempotency, completely defines the $\mathbf{P}$ matrix. The position of a floating spherical Gaussian orbital with respect to the Be atom (all other symmetry-related floating Gaussian orbitals are positioned by the operations of the group D_{3h}) is $R=1.70(3)$ Å, $\theta=26.1(18)°$, and $\phi=63.4(10)°$. The angles θ and ϕ are measured from the planes (010) and (001), respectively. The exponent scale for these floating Gaussian orbitals is $\alpha=1.38(14)$ Å^{-2}. Our overall x-ray scale factor is $S=1.0087(13)$, which matches closely the absolute scale factor of 1.007(3) determined by Larsen and Hansen. Our maximum extinction correction is 0.9972 for the 002 reflection. Our thermal parameters $U_{11}=0.00615(3)$, $U_{33}=0.00536(3)$ Å^2, and $U_{111}=0.0004(9)$ Å^3 are very close to Larsen *et al.*'s corresponding values 0.00597(3), 0.00540(3), and 0.0009(4) determined by neutron scattering. We mention that our thermal parameters have been treated on an equal footing with every parameter in the model, and that *all* of the scattering data have been used for determination of *all* of the parameters.

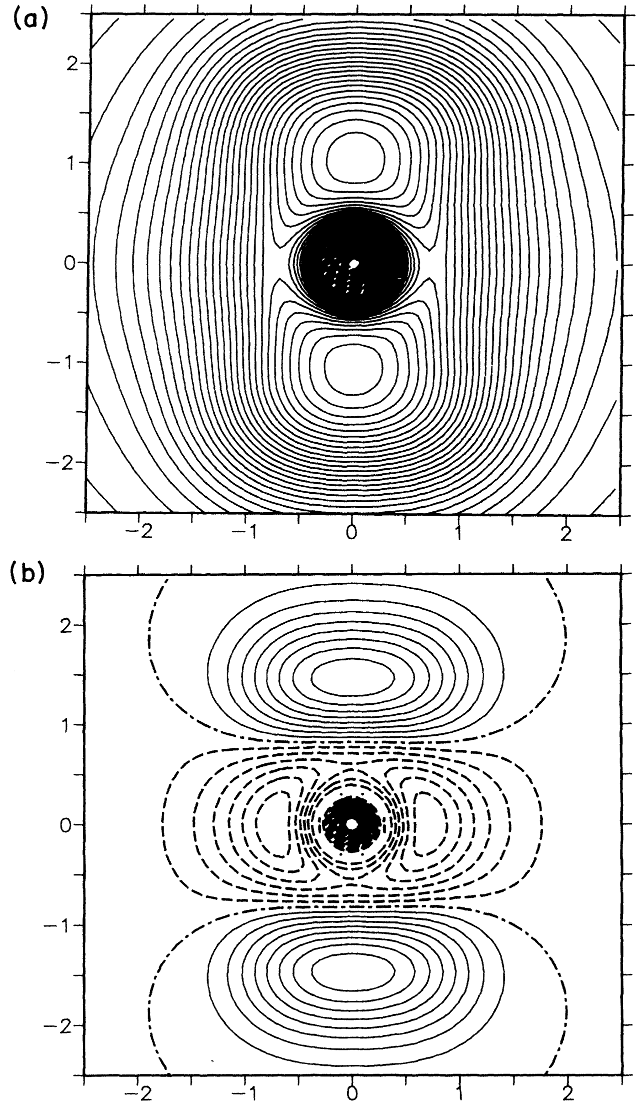

FIG. 1. (a) Valence wave function and (b) model deformation density for the hybrid Be atom. Contour interval is 0.01 Å$^{-3/2}$ (e/Å^3) for wave function (density). Positive contours, solid; zero, dot-dashed; negative, dashed. Axes are in angstroms.

In Fig. 1, for the (110) plane with z direction vertical, we display our model contours of the valence orbital, and of the deformation density obtained as the difference of the full electron density calculated from our quantum model less the electron density of a free spherical Be atom. One of the important aspects of the quantum model used here is, in fact, that the orbitals are recoverable from the fit to the scattering data. This is also related to another important point, viz; that our electron density will always be positive definite since it is directly obtained from squares of such orbitals. This is in contrast to other methods of diffraction analysis which can be plagued with negative-density features. As expected, Fig. 1(a) shows that the valence orbital peaks at the beryllium nucleus. The nonspherical features of the valence orbital are clearly evident in additional maxima along the z axis.

It is to be realized that the effects of crystal bonding on the atomic fragments are preeminently reflected in just such features of the hybrid valence orbital. Moreover, every quantum property expectation value $\langle \hat{o} \rangle$ of the fragment is available from its orbitals (within the single-determinant restriction, and will conform to the usual bounds implied by such an approximation) since $\langle \hat{o} \rangle = 2\,\mathrm{Tr}\langle \boldsymbol{\phi} | \hat{o} | \boldsymbol{\phi} \rangle$. (Here $\hat{o}$ is at most a sum of one-body operators. Although two-body operator expectation values assume a different form than that indicated here, in a single-determinant approximation they too are available from the orbitals.) From the orbitals flow *all* expectation values, but not from the density alone. Whereas the methods of accurate diffraction analysis currently and commonly in use yield an analytic expression for the density alone, not related to orbitals (or wave functions), this last point is to be emphasized as crucially in favor of our method. To give a specific example, a fragment property such as its kinetic energy is represented by the quantum operator $\hat{T} = -\frac{1}{2}\nabla^2$ (an operator which is not simply multiplicative) and has the expectation value $\langle \hat{T} \rangle = 2\,\mathrm{Tr}\langle \boldsymbol{\phi} | -\frac{1}{2}\nabla^2 | \boldsymbol{\phi} \rangle$, which can be easily evaluated given the orbitals $\boldsymbol{\phi}$ (again we emphasize, within the single-determinant approximation). The general matrix element in the trace is

$$\langle \phi_i | -\tfrac{1}{2}\nabla^2 | \phi_i \rangle = \int \phi_i(r)(-\tfrac{1}{2}\nabla^2)\phi_i(r')|_{r' \to r}\, d^3r,$$

where is it understood in Löwdin's notation that $-\frac{1}{2}\nabla^2$ operates on the primed coordinates first, after which they become unprimed and integration takes place. However, given the density $\rho(r)$ alone one cannot in a similar way evaluate the expectation value $\langle \hat{T} \rangle$. In the density $\rho(r)$, primed and unprimed coordinates have no individual significance (i.e., $r' \equiv r$) and the *usual* procedure just given for evaluating $\langle \hat{T} \rangle$ cannot be applied. The only property expectation values that can be obtained from the density alone are those represented by operators which are purely multiplicative such as various powers of the distance r. For these cases the general rule for evaluating expectation values collapses to an expression requiring the density alone, e.g.,

$$\int \sum \phi_i(r) r \phi_i(r')|_{r' \to r}\, d^3r = \int r \rho(r)\, d^3r.$$

Now, using the valence orbital of Fig. 1(a) (and the fixed $1s$ core) we have calculated four interesting expectation values for both the Be hybrid atom and the free atom. These are the electron-nuclear attraction energy, the average electron distance—measured from the nucleus, the average squared distance—a factor in the quadrupole moment of a charge distribution, and the electronic kinetic energy. The magnitudes of these expectation values, hybrid (free), in atomic units are, respectively, $\langle -zr^{-1} \rangle = -31.6608$ (-33.2340), $\langle r \rangle = 7.8409$ (6.1259), $\langle r^2 \rangle = 19.1857$ (17.2820), and $\langle -\frac{1}{2}\nabla^2 \rangle = 13.6911$ (14.5720). The magnitudes of the hybrid Be properties are reasonable. In particular, the kinetic energy is less than the free-atom value as is anticipated if the electron distribution "occupies" more space in the crystal versus the free atom. But in accordance with our previous discussion, the important point demonstrated numerically is that even such nonmultiplicative properties as the kinetic energy are available from our method since we obtain a density matrix in an orbital representation. This is not the case for methods of diffraction analysis which give the density alone.[6]

The nonsphericity of the Be hybrid atom is evident in the model deformation density of Fig. 1(b). One may interpret the figure as the charge rearrangement of an atom due to crystal bonding. Charge coming from along the horizontal axis and out of the core region flows along the vertical axis. Hence, a clear anisotropy is established when the c direction is compared to the a or b directions. Indeed, the hybrid's charge buildup along c is consistent with the Be crystal's ratio of $c/a = 1.568$ which is 3% below the ideal value for hexagonal close packing of 1.633. If the bonding along c is stronger than along a or b, and that is indicated by the deformation density, then the natural consequence is shortening along c, and, hence, a reduced value of c/a compared to the ideal case.

If one superposes the deformation density of all Be hybrid atoms, each Be at its position in the lattice, one obtains the model deformation density of the crystal as a whole. We have carried this out graphically superposing the effects of 500 hybrid atoms contained in 125 orthohexagonal unit cells. The result, which conforms quantitatively to the experimental deformation maps of Larsen and Hansen,[2] is that charge flows into the tetrahedral hole regions and out of the nuclear regions and octahedral channels. Bonding, therefore, is directed through the tetrahedral holes. Interestingly, examination of the deformation density of the crystal has been interpreted as a bonding scheme based upon resonating sp^3 orbitals directed toward tetrahedral holes. However, our hybrid deformation density from which the full crystal deformation is constructed is not consistent with a sp^3 hybrid scheme.

The basis we have used relies upon floating spherical Gaussian orbitals to represent the nonspherical components of the Be hybrid atom's orbital. If one wished to analyze our deformation density in terms of more commonly used basis orbitals, Fig. 1(b) would be consistent with an orbital having a much larger p_z character than an sp^3 hybrid.

Figure 2 presents our model valence-density map for the $(X, Y, \frac{1}{4})$ crystal plane. Corresponding *ab initio* results are shown for comparison. The results of Dovesi *et al.*,[7] Fig. 2(a), are based upon *ab initio* Hartree-Fock linear combination of atomic orbitals cal-

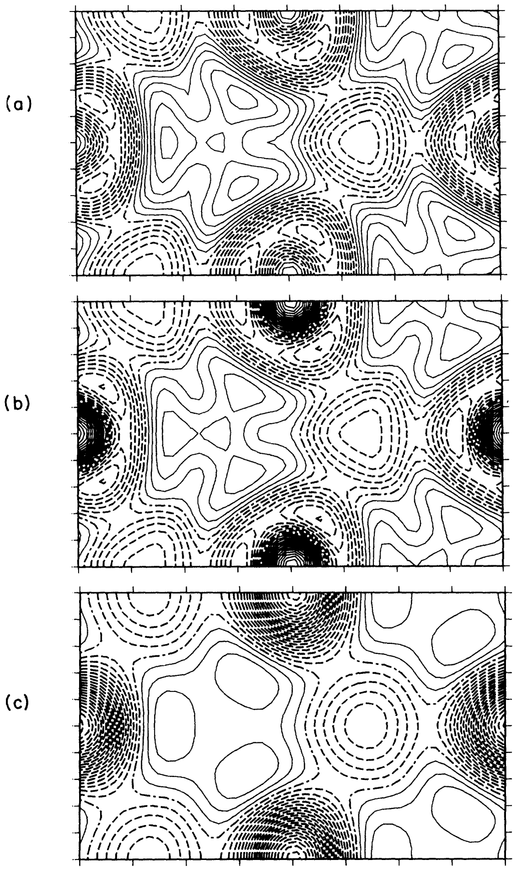

FIG. 2. Valence density from (a) Dovesi *et al.*, (b) this work, and (c) Chou, Lam, and Cohen. Projections of the tetrahedral and octahedral holes are indicated. Contour intervals are as in Fig. 1 except that the zero contour refers to four electrons per unit cell volume.

culations using an extended basis of *s* and *p* functions. Our work is shown in Fig. 2(b). The results of Chou, Lam, and Cohen,[8] Fig. 2(c), are *ab initio* pseudopotential calculations within the local-density-functional scheme. Both of the *ab initio* methods shown here have been widely applied to solids and are capable of yielding reliable results. All three maps in Fig. 2 have been generated by Fourier summation of 28 thermally smeared structure factors. In each case, the neutron thermal parameters of Larsen and Hansen[2] have been used. On the whole, the concordance between *ab initio* and x-ray orbital valence-density features is excellent. The nonspherical aspects of the valence density are clearly apparent. Completely in agreement with the experimental maps of Larsen and Hansen[2] there is a buildup of charge around the tetrahedral hole regions at the expense of charge removed from the crystal's octahedral channels. Our map agrees quantitatively more closely with the experimental map of Larsen and Hansen,[2] and like theirs falls numerically between the two *ab initio* maps shown.

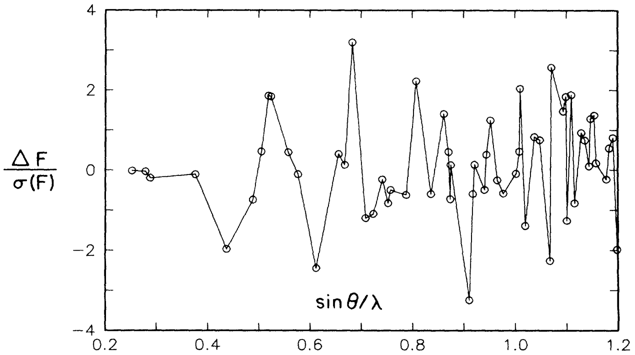

FIG. 3. Distribution of errors. $R_{WF} = 0.0018$, and G.O.F. = 1.33.

In Fig. 3, in order to analyze how well our model represents the experimental data, we plot ΔF, the difference between observed and calculated structure factors, in units of σ (the standard deviation of F) as a function of scattering angle. The model is seen to fit the highly accurate Be data remarkably well. Notice that the errors in F are randomly distributed out to highest angles in close accordance with a normal distribution of errors. The weighted R factor has the very small magnitude 0.0018 and is calculated with use of weighting factors that are based solely upon the counting and sample variance statistics of the experiment. The goodness of fit, G.O.F. = 1.33, is another indicator that our model matches the experiment very well. Indeed, the excellent fit over the full range of $\sin\theta/\lambda$ obtained with the very simple orbital model used here is satisfying.

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[(a)] Permanent address: School of Theoretical and Applied Science, Ramapo College, Mahwah, N.J. 07340.

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