Wave Function for Beryllium from X-Ray Diffraction Data

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We describe a procedure to extract a single determinant wave function from x-ray charge density structure factors. The orbitals obtained can be seen as Hartree-Fock orbitals constrained to give the experimental density to a prescribed accuracy. The method is applied to beryllium metal. From our wave function we extract the binding energy and work function for the crystal. Both are in qualitative agreement with independent experiments. There is no evidence for non-nuclear maxima in the charge density. [S0031-9007(97)04985-5]

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In some interesting recent work, Zhao, Morrison, and Parr [1] have obtained the Kohn-Sham wave function of density functional theory from a *theoretical* electron density distribution. They observed that for the Be atom, the Kohn-Sham orbitals were nearly indistinguishable from the Hartree-Fock orbitals. On this evidence, they claim that the problem of finding a physically meaningful model wave function from an electron density is "solved."

In this Letter, we derive a model wave function from *real* charge densities measured using x-ray diffraction experiments on the beryllium system. Although there is a long history associated with this problem [2–6], the use of model wave functions in physics (as distinct from model Hamiltonians) is surprisingly undeveloped, given their promise for understanding and enhancing the quality of first principles calculations. The idea used here is conceptually simple and general: we extract the determinant which yields the observed electron density and minimizes the Hartree-Fock energy. (The Kohn-Sham determinant, on the other hand, yields the electron density and minimizes the kinetic energy [1].) Our particular interest in beryllium is motivated by recent claims [7,8] that there are regions in the electron density, not at a nucleus, which are local maxima. Such maxima have never been observed previously in nature.

There are a number of nice features for the model wave function proposed here. First, it is unique [6,9]. Second, the problem of having sufficient data does not arise, unlike other methods [2,5]. Also, the model maintains all the elements of a first principles quantum mechanical calculation; comparisons between theory and experiment are greatly facilitated since nearly the same methods are used in both. Further, the Hartree-Fock model is known to give very reliable results for electron densities. However, two new issues need to be considered when using real data. First, because of experimental errors, we should not constrain our wave function to exactly produce the experimental charge density. Second, because we use data for a periodic system, the orbitals must be constrained to be orthogonal throughout the crystal if we want to get a reasonable wave function for the system. The resolution of the orthogonality problem is not critical for the purposes of charge density modeling, but will allow useful formal theoretical results to be used.

We begin by reviewing the method of Zhao and Parr [1]. Consider a single determinant wave function whose orbitals ϕ_i are obtained from a model Hamiltonian h,

$$h\phi_i = \left(-\frac{1}{2}\nabla^2 + v\right)\phi_i = \epsilon_i\phi_i\,. \tag{1}$$

The density is given by

$$\rho(\mathbf{r}) = 2\sum_i^{N_e/2} |\phi_i(\mathbf{r})|^2. \tag{2}$$

If ρ is constrained to be the same as the exact ground state density ρ_0, then the orbitals will satisfy the equation

$$h_{\text{eff}}\phi_i = (h + \lambda v_c)\phi_i = \epsilon_i\phi_i\,, \tag{3}$$

where λ is the Lagrange multiplier attached to the constraint. The form of v_c depends on the specific choice of the constraint (or penalty) function [1]. Provided the potential v is local in $\mathbf{r}$, in the limit that $\lambda \to \infty$ we will have $\rho \to \rho_0$ *independent of the choice of* v. In this limit, then, Eq. (3) gives the Kohn-Sham orbitals and eigenvalues. The determinant formed from these orbitals is a wave function obtained from the density ρ_0.

The constraint function used here to force charge density to be the same as experiment is the χ^2 statistic,

$$\chi^2 = (1/M)\sum_{\mathbf{h}}(F_{\mathbf{h}} - F_{\mathbf{h}}^c)^2/\sigma_{\mathbf{h}}^2\,, \tag{4}$$

often used in crystallography as a measure of error. $F_{\mathbf{h}}$ and $F_{\mathbf{h}}^c$ are, respectively, the observed and calculated structure factors, $\sigma_{\mathbf{h}}$ is the error associated with each measured structure factor $F_{\mathbf{h}}$, and M is the number of observations. The structure factors are related to the unit cell charge density by a Fourier transform,

$$F_{\mathbf{h}} = \int \rho^{\text{cell}}(\mathbf{r})\exp(2\pi i\mathbf{r}\cdot\mathbf{Bh})\,d\mathbf{r}\,, \tag{5}$$

where $\mathbf{B}$ is the reciprocal lattice matrix dependent only on the crystal morphology, and $\mathbf{h}$ is an integer vector (the Miller indices) labeling the reflection. An important point to note is that χ^2 is not forced to be zero: it does not make sense to exactly reproduce an experimental density which contains errors. Instead, χ^2 is constrained to be equal to a certain value ξ_p. One obvious choice for ξ_p is 1, so that calculated structure factors are (on average) within one standard deviation of experiment. A more rigorous choice could be as follows. First, assume that the distribution of squared residuals is normal, as is often done in crystallography. Then tables are available [10] which give the probability p that a particular experiment will give a χ^2 less than ξ_p. The value of ξ_p can be chosen according to the desired confidence level p. Of course, other ways to choose ξ_p are possible, as are other choices for the agreement statistic.

As a consequence of the nonzero value demanded for the χ^2 statistic, the solution to (3) (if possible at all) will occur at a *finite* value of λ. Because of this, the choice of v is no longer arbitrary. Clearly, v must be chosen using the best possible model, so that one does not have to constrain the orbitals very much to obtain the observed charge density. The Hartree-Fock (HF) model is chosen for this work, $v = v^{\mathrm{HF}}$, because studies have already indicated that very good results are obtained at this level [11], and, as already noted, the HF orbitals appear to be very similar to the Kohn-Sham orbitals for the case examined here, beryllium. It should be noted, however, that the Hartree-Fock potential is that it is not a local potential. In the case of perfect data (i.e., zero experimental error), the fitted orbitals obtained are no longer Kohn-Sham orbitals, as they would have been if a local potential had been used [1].

To calculate the crystal structure factors we restrict our attention to systems which are centrosymmetric (so the structure factors are real) and composed of one symmetry unique molecule in each unit cell. Then the cell charge density can be decomposed into a sum of N_m molecular charge densities ρ^j, each related by unit cell symmetry operations $\{\mathbf{S}_j, \mathbf{r}_j\}$ to a reference charge density for the molecule ρ^0,

$$\begin{aligned} \rho^{\mathrm{cell}}(\mathbf{r}) &= \sum_{j=1}^{N_m} \rho^j(\mathbf{r}) , \\ \rho^j(\mathbf{r}) &= \rho^0[\mathbf{S}_j^{-1}(\mathbf{r} - \mathbf{r}_j)] . \end{aligned} \tag{6}$$

It is usually a good approximation to take ρ^0 to be the isolated molecule charge density, but within the above restrictions, no approximation has yet been made. For practical calculations ρ^0 is usually obtained in a basis set. If we write

$$\phi_i = \sum_\mu c_{\mu i} g_\mu , \tag{7}$$

then, using (2), the reference molecule charge density basis set expansion is

$$\rho^0(\mathbf{r}) = \sum_{\mu,\nu} D_{\mu i} g_\mu(\mathbf{r}) g_\nu(\mathbf{r}) , \tag{8}$$

where $D_{\mu\nu} = 2 \sum_i^{N_e/2} c_{\mu i} c_{\nu i}$ is the (closed shell) density matrix. Using this in (6) and substituting in (5), we have the desired result for the calculated structure factors,

$$F_{\mathbf{h}}^c = \mathrm{Tr}(\mathbf{D I_h}) . \tag{9}$$

$\mathbf{I_h}$ are the Fourier transforms of the basis function pairs summed over all the equivalent unit cell sites,

$$\begin{aligned} I_{\mu\nu,\mathbf{h}} = &\sum_j^{N_m} \exp(2\pi i \mathbf{r}_j) t_{\mu\nu}((\mathbf{B})^{-1}\mathbf{S}_j^T \mathbf{Bh}) \\ &\times \int g_\mu(\mathbf{r}) g_\nu(\mathbf{r}) \exp(2\pi i \mathbf{r} \cdot \mathbf{B}[(\mathbf{B})^{-1}\mathbf{S}_j^T \mathbf{Bh}])\, d\mathbf{r} . \end{aligned} \tag{10}$$

Fast methods for evaluating these integrals for the case of Gaussian basis functions are known [12]. Also, Hall has described how to get the symmetry operators $\{(\mathbf{B})^{-1}\mathbf{S}_j^T \mathbf{B}, \mathbf{r}_j\}$ for any crystal space group [13]. The parameters $t_{\mu\nu}$ account empirically for thermal smearing of the charge density. We use the form recommended by Stewart [14],

$$t_{\mu\nu}(\mathbf{h}) = \exp[-2\pi^2 g(\mathbf{Bh}) \cdot (\mathbf{U}^\mu + \mathbf{U}^\nu)\mathbf{Bh}] , \tag{11}$$

which are expressed in terms of the thermal vibration parameters $\mathbf{U}^\mu$ (also obtained from the x-ray experiment) for the atom on which basis function g_μ is centered. The factor g is $\frac{1}{2}$ if the motions of atoms μ and ν are "correlated," or $\frac{1}{4}$ if "uncorrelated." In this work, atoms were deemed correlated if they were less than 2.5 bohr apart. Different thermal smearing models have been proposed [15], but in practice the differences are small. Additional $\mathbf{h}$ dependent factors which account for extinction may also be incorporated in (10), but were not used here. However, an overall ($\mathbf{h}$ independent) scale factor was used, since the absolute scale is not always well defined in the x-ray experiment.

To construct a determinant for the entire crystal, the orbitals we extract for one molecule in the crystal must be orthogonal to all other orbitals on all other molecules in the crystal. To ensure the required orthogonality, a projection operator is used

$$\kappa \sum_k^{\text{neighbors}} |\phi_i^k\rangle\langle\phi_i^k| . \tag{12}$$

It is assumed that the orbitals on the reference system ϕ_i are fairly localized. All the other orbitals in the crystal ϕ_i^k are related to the reference orbitals by translations and crystal symmetry operations as in (6). The assumption of locality means that only a finite number of neighbors near to the reference molecule need be included in the above summation. Adding the above projector to any equation for the reference system orbitals and choosing the Lagrange multiplier κ large enough will ensure orthogonality; the parts of the orbitals which are not orthogonal become energetically unfavorable, and are thus removed.

The matrix form for (3) expressed in a finite basis set with the various constraints described above is easily shown to be

$$\tilde{\mathbf{f}}\mathbf{c} \equiv (\mathbf{f} - \lambda \mathbf{v}_c + \kappa \mathbf{p})\mathbf{c} = \mathbf{S}\mathbf{c}\boldsymbol{\epsilon} , \tag{13}$$

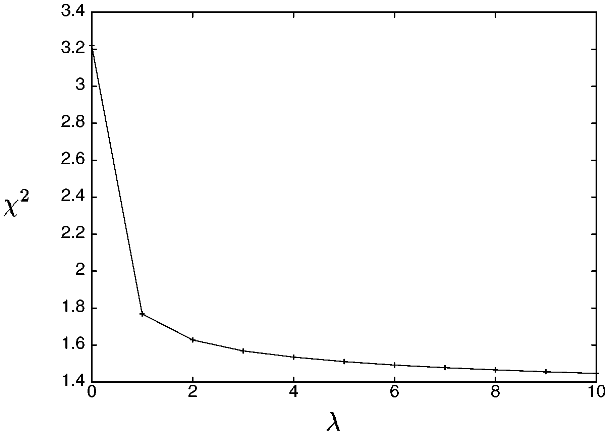

FIG. 1. χ^2 agreement statistic for the x-ray structure factors vs Lagrange fitting parameter λ.

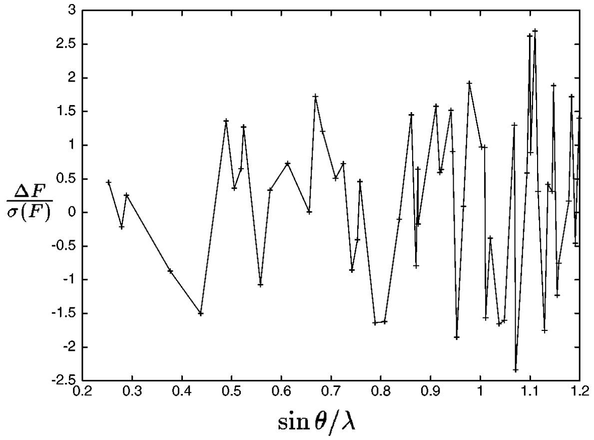

FIG. 2. Relative errors in fitted structure factors as a function of scattering angle.

where $\mathbf{S}$ is the overlap matrix, $S_{\mu\nu} = \langle g_\mu | g_\nu \rangle$ and $\mathbf{f}$ is taken to be the Fock matrix in this work, $f_{\mu\nu} = \langle g_\mu | -\frac{1}{2}\nabla^2 + v^{\mathrm{HF}} | g_\nu \rangle$. The matrix of the χ^2 constraint term $\mathbf{v}_c$ is given by

$$\mathbf{v}_c = (2/M) \sum_{\mathbf{h}}^{M} (F_{\mathbf{h}} - F_{\mathbf{h}}^c) \mathbf{I}_{\mathbf{h}} / \sigma_{\mathbf{h}}^2 . \tag{14}$$

The matrix of the projection term $\mathbf{p}$ which ensures orthogonality to neighboring molecules is

$$\mathbf{p} = \sum_{k}^{\text{neighbors}} (\mathbf{S}\mathbf{c}^k)(\mathbf{S}\mathbf{c}^k)^T . \tag{15}$$

These equation are solved in the usual self-consistent way, the Lagrange multipliers λ and κ being chosen large enough to give, respectively, the desired agreement with experiment, or the desired orthogonality to near neighbors. As for normal HF equations, there will be $N_e/2$ "occupied" orbitals $\mathbf{c}_o$ and a number of "virtual" orbitals $\mathbf{c}_u$, with $\mathbf{c} = (\mathbf{c}_o \mathbf{c}_u)$.

In practice, convergence problems are observed, because as λ becomes larger, $\mathbf{f}$ becomes small compared with $\mathbf{v}_c$, and the solution of (13) becomes like a least squares fit, which is a singular problem if there are less data than parameters. Using real data with normal basis sets, $\mathbf{v}_c$ is unlikely to go to zero as λ gets larger, so the equations become increasingly ill-conditioned. The convergence acceleration technique of Pulay [16] improves the situation. Alternatively, Eq. (13) can be recast as follows: The occupied-occupied and virtual-virtual block of $\tilde{\mathbf{f}}$ are arbitrary and can be scaled by λ. Now divide the scaled $\tilde{\mathbf{f}}$ in (13) by λ and substitute $\epsilon/\lambda \rightarrow \epsilon$ and $\kappa/\lambda \rightarrow \kappa$ (we can do this because they are Lagrange multipliers). We then obtain

$$\tilde{\mathbf{f}}^\lambda \mathbf{c} = \mathbf{S}\mathbf{c}\boldsymbol{\epsilon} , \tag{16}$$

where $\tilde{\mathbf{f}}^\lambda$ has had its occupied-unoccupied blocks scaled by $1/\lambda$,

$$\mathbf{c}^T \tilde{\mathbf{f}}^\lambda \mathbf{c} = \mathbf{c}_o^T \tilde{\mathbf{f}} \mathbf{c}_o + \mathbf{c}_v^T \tilde{\mathbf{f}} \mathbf{c}_v + \frac{1}{\lambda} (\mathbf{c}_v^T \tilde{\mathbf{f}} \mathbf{c}_o + \mathbf{c}_o^T \tilde{\mathbf{f}} \mathbf{c}_v) . \tag{17}$$

The theory described in the previous section is now applied to beryllium metal. Accurate low temperature data were taken from the paper of Larsen and Hansen [17]. [But note that in (14) I used the structure factors multiplied by 1000, as given in their paper.] For the orthogonalization, the first shell of nearest neighbors was used. There were 12 atoms. A "triple-zeta" basis set from Ref. [18] was used. There are 182 basis functions and 361 independent parameters in the wave function, whereas there are 58 experimental measurements. Figure 1 shows a plot of the χ^2 agreement statistic as a function of the parameter λ, for $\kappa = 0.2$. Larger values of κ caused numerical instability. For $\lambda = 10$ the overlap with the near neighbors was 0.004 and 0.002 for κ equal to 0.1 and 0.2, respectively. The plot for $\kappa = 0.1$ is indistinguishable on this scale. The value of χ^2 at $\lambda = 10$ was 1.44, with the overall scale factor being 0.997. A straight atomic density gave a χ^2 of 2.37: the atomic model is already very good. It seems clear that a χ^2 much lower than 1.44 is not practically obtainable, either because the energy penalty is too high, or the basis set is inadequate. To test the latter, calculations were performed with an additional d function (exponent 0.32 atomic units) on the beryllium atom, but to make the calculations practical, orthogonalizing the orbitals to the near-neighbors was not performed. (This approach corresponds to using up to $l = 4$ in a normal least squares multipole moment approach.) The value of χ^2 obtained was 1.40, indicating the basis set is not the problem. A scatter plot in Fig. 2 as a function of scattering angle shows that the deviations of the fitted results are random. There are no obvious systematic errors. Figure 3 is a plot of the thermally smeared deformation densities, calculated from our structure factors. Interestingly, there is hardly any buildup of electron density in the tetrahedral and octahedral hole positions of the hexagonal close packed structure. However, there are depletions of charge similar to those observed by Larsen and Hansen [17], in plots that they give which are derived from Fourier summation techniques. There is no evidence in this model for non-nuclear maxima in the charge density [7,8].

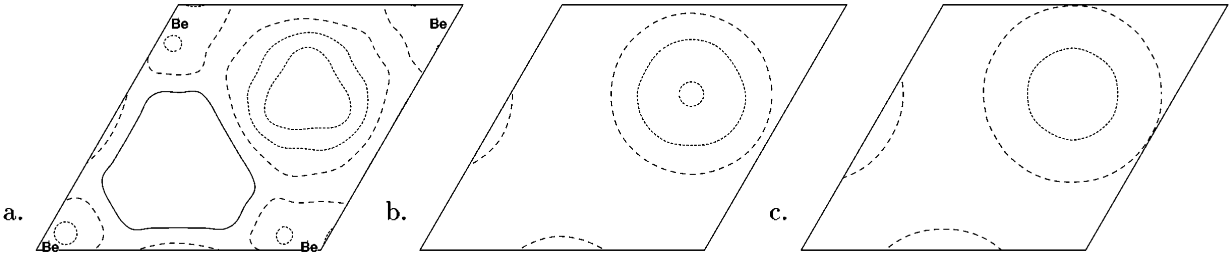

FIG. 3. Thermally averaged electron deformation density for Be crystal. Section (a) at $z = 0.75$, the basal plane, (b) at $z = 0.625$, containing the tetrahedral hole site, and (c) at $z = 0.5$, containing the octahedral hole site. Origin is at the top left corner; z is the fractional coordinate along axis c; axes a and b increase across and down the page, respectively; contours interval is 0.015 e/bohr^3; dotted lines are negative, solid lines are positive.

Now to more interesting properties that can be extracted in our approach which cannot be extracted in a standard x-ray charge analysis. For a system at equilibrium, the virial theorem gives the total energy as $E = -T$. The "noninteracting" kinetic energy T_s from our determinant is 14.7861 a.u. for $\lambda = 10$, $\kappa = 0.2$. From this and the exact result for the Be atom ground state energy of -14.6674 a.u. [19], a binding energy of 312 kJ/mol is obtained. At $\lambda = 5$ and $\kappa = 0.2$, the binding energy is 390 kJ/mol. The observed value is 318 kJ/mol [20]. However, it should be noted that the error $T_c = T - T_s$ in the Kohn-Sham theory is known to be 194 kJ/mol for the Be atom [1].

An approximate ionization energy or work function can also be extracted. In density function theory, the ionization energy is given by the highest eigenvalue [21], which is governed by the long range behavior of the density. If our fitted orbitals are a good approximation to the Kohn-Sham orbitals, they can be used to define the highest eigenvalue for an *approximate* one-particle effective potential. With three popular choices, the Hartree-Fock potential, the local density approximation (comprising Dirac's exchange [22] plus local correlation energy functional of Ref. [23]), and the "BLYP" approximation (comprising the Becke exchange functional [24] plus correlation functional from [25]), the results are, respectively, 6.0, 3.7, and 4.9 eV. These are to be compared with the experimental value of 4.98 eV [20]. Even though there is a considerable spread in the results, as expected for such a crude calculation, they are all better than the free atom Hartree-Fock value of 8.4 eV. From these results it would seem our fitted wave function is not unreasonable.

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