

# Modeling of Numerical Atomic Electron Density Data with Analytical Functions

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An approach is presented for developing analytical models of user-defined atomic electron-density data. In place of tabulated data, modified Slater-type wavefunctions are used to describe ions and atoms. The desired charge distribution is obtained by adjusting orbital exponents, with orbital coefficients kept fixed to help maintain normalized functions. The analytical functions obtained by the fitting procedure are identical in form to standard Hartree–Fock wavefunctions, permitting the model functions to serve as input for Gordon–Kim electron gas calculations. For such work, Slater-orbital wavefunctions are used to calculate the electrostatic potential and electron density of ions in solids. The modeling procedure permits one to modify the character of an ionic charge cloud without resorting to numerical data. The approach is illustrated for the  $O^{2-}$  ion; analytical functions are derived on the basis of a number of treatments: the standard closed-shell ion, a “hybridized” valence state, and empirical data.

## INTRODUCTION

The Hartree–Fock treatment of the Schrödinger equation is widely used to explore the quantum chemistry of gas-phase ions and atoms. Wavefunctions may be based on Slater-type orbitals or Gaussian-type functions. Both methods provide reliable models of the electronic orbitals, total energy, and electron density of spherically symmetric systems. The self-consistent-field energy minimization process determines the wavefunction and hence defines the shape (and size) of the electron charge cloud.

Though adequate for many lines of study, analytic wavefunctions are not ideal for all work. Analysis of experimental diffraction data yields charge density in terms of charge/unit volume. Theoretical methods use a variety of quantum mechanical electron-density models: standing waves, scattered waves, and wavefunctions. Ideally, our approach should be flexible enough to permit its use for any of these applications.

One method of particular interest, the Gordon–Kim electron gas approach, models the electron density of a solid with ionic charge densities placed on the appropriate lattice sites.<sup>1</sup> Hartree–Fock wavefunctions are suitable for ionic solids; i.e. all ions exhibit closed-shell electronic structure.<sup>2</sup> However, one faces a dilemma if standard wavefunctions are unavailable or inappropriate for the problem. Such is the case for open-shell atoms<sup>3</sup> or solids displaying significant covalent character.<sup>4</sup> In each instance the theoretical treatment must be modified to treat these non-ionic or open-shell systems. The net result is that a total reliance on Hartree–Fock wavefunctions limits the systems which can be accurately studied with electron-gas methods.

As an alternative to Hartree–Fock wavefunctions, ionic charge densities can be described using numerical (non-analytical) data derived from experiment or other theoretical models. However, working with tabular numerical data presents a number of practical problems. One must determine the number and location of points required to accurately describe the behavior. In addition, small fluctuations at each point may introduce error in the normalization (total charge) and electrostatic potential. The long-range behavior must be carefully handled since the electron-density must converge to “zero” in a smooth fashion. More importantly, relatively small errors in the numerical input gives rise to much larger errors in the properties derived from the electron density, such as

electrostatic potential, total charge, and non-point Coulomb interactions between pairs of ions.

Therefore, a systematic, analytical fit of the numerical data may in fact be more useful than the actual data. For this reason, we have developed an approach for modeling numerical charge data with wavefunction-type analytical functions.

## COMPUTATIONAL METHOD

In order to derive an analytical model of numerical charge data, one must first choose the specific features used to describe the ion. In this work, two characteristics of a spherically symmetric charge cloud are used to guide the fitting procedure: the electron density,  $\rho_i = 4\pi r_i^2 \rho(r_i)$ , at a number of distances  $\{r_i\}$  and the total electronic charge,  $q_{tot,i}$ , contained by each of the concentric spheres of radius  $r_i$ . If desired, other properties of the wavefunction, such as  $\langle r \rangle$ ,  $\langle r^n \rangle$  or  $\langle r^{-n} \rangle$ , can be used as easily as  $\rho_i$  and  $q_{tot,i}$ .

The goal of our method is to provide a flexible, yet quantitative, description of the shape of the ionic charge cloud. The fitting procedure could be performed solely on the basis of the charge density data ( $\{\rho_i\}$ ) or the total accumulated charge at each of the prescribed radial distances ( $\{q_{tot,i}\}$ ). The former may be desirable for the modeling of experimental charge densities, obtained from X-ray data. The latter permits examination of relationships between ion size and effective charge. Consideration of both features provides maximum flexibility in choice of the  $r_i$  values and provides a check of the normalization of the ionic charge.

An analytical model of ionic charge could take a variety of forms, within the limits of the boundary conditions of the problem. In the current work, a form equivalent to a Slater-type wavefunction<sup>2</sup> is chosen in order to yield a standard description of the ionic charge. A full description of the orbitals comprising an asymmetric Slater-type Hartree–Fock wavefunction is given in the Appendix. Each fully-occupied orbital (1s, 2s, or 2p) is described with a linear combination of Slater functions having the appropriate radial and angular behavior. For our purposes, this choice also facilitates interfacing with solid-state Gordon–Kim electron-gas calculations. This option has the added advantages of providing flexibility—one can use a simple or rigorous Slater-orbital basis set—and the new functions are easily compared with standard wavefunctions.

In the optimization procedure, only the Slater-function exponents are varied. The Slater-orbital coefficients are held

**Table I.** Analytic Fits of the  $1s^2 2s^2 2p^6$  Hermann–Skillmann  $O^{2-}$  Ion

		$r_i$ (au)							error (%)
		1.47	2.01	2.51	3.00	3.50	3.99	4.49	
Hermann–Skillmann Numerical									
$\rho_i$	3.39	2.00	1.21	0.70	0.39	0.21	0.12	0.061	
$q_{tot_i}$	6.78	8.18	8.96	9.42	9.69	9.83	9.91	9.95	
Initial Guess: Hartree–Fock SCF									
$\rho_i$	3.41	2.04	1.25	0.76	0.44	0.25	0.13	0.068	8
$q_{tot_i}$	6.66	8.07	8.87	9.36	9.65	9.82	9.91	9.96	
Fit: 8 Points									
$\rho_i$	3.38	2.03	1.19	0.69	0.39	0.22	0.12	0.059	1.4
$q_{tot_i}$	6.76	8.19	8.97	9.43	9.69	9.83	9.92	9.96	
Fit: 6 Points									
$\rho_i$	3.39	2.02	1.20	0.70	0.39	0.21			0.5
$q_{tot_i}$	6.77	8.18	8.96	9.42	9.69	9.83			
Fit: 4 Points–Tail									
$\rho_i$				0.69	0.39	0.22	0.11		0.7
$q_{tot_i}$				9.43	9.69	9.84	9.91		

constant during the process, simplifying the minimization with little loss in function flexibility and fitting accuracy. This choice also helps the program maintain normalized functions.

A Fortran program, COMPARE, calculates  $\rho$  from the Slater-type function and performs the charge density/shape optimization. The required inputs are (a) a numerical description of the ion or atom and (b) an initial guess for the analytical function. The error between the model and numerical data is minimized using an algorithm (DFMND) which locates the extrema of a function of several variables without the use of derivatives.<sup>5</sup> DFMND is used to vary the Slater exponents, thus obtaining improved descriptions of the charge density. The functions obtained by the optimization procedure are not unique. A number of functions can be derived which give rise to the same charge density. The only constraint placed on the values of the exponents is that they must be positive and the largest acceptable value is 50.00. In practical terms, any exponent larger than this yields negligible charge contribution. This constraint prevents the program from wasting time on exponents which have little effect on the final charge density.

The strategy of the fitting procedure is summarized as follows:

**Step 1.** For prescribed test distances,  $\{r_i\}$ , determine  $\{\rho_i\}$  and  $\{q_{tot,i}\}$ . This step defines the numerical description of the ionic charge cloud.

**Step 2.** Calculate the electron density and total charge at each  $r_i$  based on an initial guess for the Slater-function exponents, thus providing a zero-order analytical fit to the data given in step 1.

**Step 3.** Determine the least-squares error between the analytical and numerical values for  $\rho_i$  and  $q_{tot,i}$  corresponding to each  $r_i$ .

**Step 4.** Systematically vary the Slater exponents in the function, using DFMND, to minimize the discrepancy between the numerical and analytical charge descriptions.

Interested parties may obtain a complimentary copy of the COMPARE source-code from the author. The program package (consisting of the main control program, the sub-routines to generate charge density from Slater wavefunctions, the shape optimization algorithms, sample input, and sample output) can be obtained on IBM-compatible floppy diskette (send formatted floppy via postal mail) or through electronic mail [Internet address: JACKSONM@ACC.FAU.EDU or Bitnet address JACKSONM@FAUVAX].

## MODELING OF NUMERICAL ELECTRON DENSITY

The program described in the previous section is used to obtain analytical models of numerical  $O^{2-}$  charge data. Almost any numerical charge data can be used as input to the fitting program. For the first two examples presented in this paper the numerical electron densities are generated with the Hermann–Skillmann atomic SCF method<sup>6</sup> using a program written by Cook and Case.<sup>7</sup> These numerical wavefunctions are based on a density functional treatment of the exchange energy. This approach has the advantage of allowing the electronic configuration and net charge of the ion to be easily varied. For closed-shell ions, these electron densities are comparable to Hartree–Fock results.

As a third example of the modeling procedure, empirical oxide charge data are explored. For this work, arbitrary electron density and accumulated charge data are used to derive model functions. By fitting both electron density and accumulated charge practical limits to ion size can be evaluated.

The analytical fits for the oxide anion use a basis set of five s-type and five p-type Slater functions/exponents (the Hartree–Fock basis used in ref 2). The 1s, 2s, and 2p orbital coefficients are derived, and exponents optimized, using the Hartree–Fock atomic SCF method with the oxide ion stabilized by a Watson sphere of charge +2.<sup>8</sup> These exponents serve as the initial variables for the optimization program COMPARE. As will be noted in a following section, less rigorous basis sets can be used (such as “single- $\zeta$ ”), but these result in less accurate models.

**Example 1: Standard Closed-Shell Oxide Ion.** The Hermann–Skillmann electron-density data for a closed-shell  $O^{2-}$  ( $1s^2 2s^2 2p^6$ ) is given in Table I. The tabulation covers eight test distances (ranging from 1.47 to 4.98 au) and accounts for more than 99% of the oxide electron density.

The Hartree–Fock  $O^{2-}$  wavefunction is the initial guess for the analytical fit of the numerical data. The average error associated with this initial fit is 8%. An optimization of the orbital exponents (given in Table III) brings the model charge-density and accumulated-charge data into very good agreement with the numerical data (1.4% error). Most of the error is associated with the points in the diffuse tail regions of the charge cloud. One can also model the numerical data with test points chosen from the core or tail region, as noted in Table I. These fits give smaller errors than the treatment which uses all of the test points. Therefore, if one is interested in modeling the charge density nearer the nucleus (the core)

**Table II.** Analytic Fits of the  $1s^2 2s^2 2p^5 3s^1$  Hermann–Skillmann  $O^{20}$  Ion

	$r_i$ (au)										error (%)
	1.47	2.01	2.51	3.00	3.50	3.99	4.49	4.98	6.05	7.04	
	Hermann–Skillmann Numerical										
$\rho_i$	3.09	1.65	0.95	0.60	0.42	0.33	0.27	0.22	0.14	0.08	
qtot $_i$	6.66	7.88	8.51	8.88	9.13	9.31	9.46	9.58	9.76	9.87	
	Initial Guess: Hartree–Fock SCF										
$\rho_i$	3.40	2.04	1.25	0.76	0.44	0.25	0.13	0.07	0.01	0.00	38
qtot $_i$	6.66	8.07	8.87	9.36	9.65	9.82	9.91	9.96	9.99	10.0	
	Fit: 10 Points										
$\rho_i$	2.93	1.49	0.89	0.65	0.53	0.43	0.34	0.26	0.13	0.06	14
qtot $_i$	6.59	7.72	8.29	8.67	8.96	9.19	9.38	9.53	9.73	9.82	
	Fit: 8 Points										
$\rho_i$	3.00	1.53	0.93	0.66	0.50	0.37	0.27	0.18			8
qtot $_i$	6.70	7.86	8.44	8.83	9.12	9.33	9.49	9.60			
	Fit: 6 Points–Core										
$\rho_i$	3.10	1.58	0.95	0.64	0.45	0.30					4
qtot $_i$	6.67	7.87	8.48	8.87	9.13	9.32					
	Fit: 3 Points–Core										
$\rho_i$	3.11	1.62	0.97								1
qtot $_i$	6.65	7.87	8.48								
	Fit: 6 Points–Tail										
$\rho_i$					0.50	0.42	0.34	0.26	0.13	0.07	16
qtot $_i$					8.65	8.88	9.07	9.22	9.41	9.51	
	Fit: 4 Points–Intermediate										
$\rho_i$			0.91	0.63	0.45	0.31					4
qtot $_i$			8.49	8.87	9.14	9.32					

**Table III.** Summary of Model Functions for  $O^{2-}$  <sup>a</sup>

Slater-Orbital Coefficients, $c_i$								
	1s	2s	2p		1s	2s	2p	
$c_1$	0.800	0.149	0.353	$c_4$	0.180	0.128	0.872	
$c_2$	0.049	0.029	0.203	$c_5$	-0.001	-0.536	0.003	
$c_3$	0.004	-0.581	-0.300					
Slater-Orbital Exponents, $\zeta_i$ :								
	SCF Hartree-Fock	H-S $p^6$	H-S $p^5s^1$	$r_{99} = 4.5$	$r_{99} = 4.0$	$r_{99} = 3.5a$	$r_{99} = 3.5b$	$r_{99} = 3.0$
s								
$\zeta_1$	8.39	10.57	30.99	12.25	9.60	50.00	2.58	50.00
$\zeta_2$	12.35	5.88	31.17	23.72	50.00	0.56	2.74	12.24
$\zeta_3$	2.93	1.90	2.00	2.78	2.82	2.34	5.08	2.42
$\zeta_4$	7.63	13.91	50.00	9.69	11.05	10.74	3.16	8.51
$\zeta_5$	1.55	1.78	2.00	1.54	3.44	1.50	1.02	1.62
p								
$\zeta_6$	2.24	2.58	2.77	2.38	3.43	3.41	1.73	2.28
$\zeta_7$	3.79	5.51	2.78	4.74	3.97	4.64	11.27	2.33
$\zeta_8$	0.73	0.80	0.70	0.74	0.98	1.13	0.84	0.49
$\zeta_9$	0.92	0.96	0.70	0.96	1.14	47.93	1.81	50.00
$\zeta_{10}$	13.43	0.06	2.77	1.76	50.00	3.16	0.89	3.46

<sup>a</sup> All functions share the same group of orbital coefficients, derived from a Hartree–Fock calculation. For the Hermann–Skillmann (H–S) data, the exponents correspond to fits using all the test points.

or further from the nucleus (the tail), these may be more appropriate.

Since the Hartree–Fock and Hermann–Skillmann methods yield similar results for the oxide anion, relatively small changes in the exponents are needed in order to bring the model function into agreement with the numerical data. A comparison of the relevant exponents in Table III (those corresponding to the first four 2p-orbital coefficients, and the fourth coefficient in particular) confirms the similarity between the two treatments of the closed-shell oxide ion. In the following section, numerical data based on a more diffuse oxide charge cloud are studied.

**Example 2:  $2p^5 3s^1$  Oxide Ion. Hypothetical Valence State.** For this second example, the Hermann–Skillmann program is used to generate a hypothetical  $2p^5 3s^1$  valence state of  $O^{2-}$ .

As shown in Table II, this ion displays a very diffuse charge cloud (compared to the closed-shell ground state). A total of ten test points must be used in order to account for this distinct change in ion size.

Using the same initial guess as for the first example, we find an average error of 38% between the numerical (Hermann–Skillmann) data and initial guess (Hartree–Fock) for the analytical function. Following optimization of the orbital exponents, this error drops to 14% on the basis of the ten-point fit. The optimized function is summarized in Table III. Ignoring the test points greater than 5.0 au improves the model, with an error of about 8%. This trend is also observed for the three- and five-point “core” fits. A six-point fit of the tail gives error comparable to the original ten-point model. Clearly, most of the error associated with fitting the electron

Table IV. Oxide Electron Densities and Accumulated Charge<sup>a</sup>

	H-S	H-F	$r_{99} = 4.5$	$r_{99} = 4.0$	$r_{99} = 3.5$ fit a	$r_{99} = 3.5$ fit b	$r_{99} = 3.0$
$\rho_i$							
$r_i$							
1.0							3.20
1.5	3.39	3.41			1.21	4.07	1.77
2.0	2.00	2.04		1.20	0.71	1.81	0.63
2.5	1.21	1.25	1.20	0.70	0.39	0.61	0.20
3.0	0.70	0.76	0.70	0.40	0.20	0.20	0.10
3.5	0.39	0.44	0.39	0.21	0.10	0.10	
4.0	0.21	0.25	0.20	0.10			
4.5	0.12	0.13	0.10				
5.0	0.06	0.07					
$q_{tot,i}$							
$r_i$							
1.0							7.80
1.5	6.78	6.66			8.96	7.68	9.08
2.0	8.18	8.07		8.95	9.43	9.11	9.64
2.5	8.96	8.87	8.96	9.41	9.70	9.67	9.83
3.0	9.42	9.36	9.42	9.68	9.84	9.85	9.89
3.5	9.69	9.65	9.69	9.83	9.90	9.92	
4.0	9.83	9.82	9.83	9.90			
4.5	9.91	9.91	9.90				
5.0	9.95	9.96					

<sup>a</sup> H-F is obtained from the Hartree-Fock Watson-sphere stabilized wavefunction. H-S is derived from Hermann-Skillmann Watson-sphere stabilized closed-shell oxide calculation.  $r_i$ ,  $q_{tot,i}$ , and  $\sigma_i$  are in atomic units.

density arises from the diffuse tails of the charge cloud.

The difference between the standard closed-shell oxide and this valence configuration is born out in the model function exponents (Table III). The dominant fourth 2p-exponent is smaller and s-exponents are larger, indicative of a more diffuse charge cloud.

**Example 3: Arbitrary Charge Data.** The size of an ion is usually defined in terms of an empirical ionic radius, derived from experimental bond distances. Our numerical modeling scheme permits the evaluation of the size of ions based solely on electron density and accumulated charge descriptions. From this perspective, the ionic radius is defined as the radial distance which encompasses a certain fraction of the total electronic charge. A commonly used value for the radii of the oxide ion is 1.40 Å (2.64 au). For purposes of this work, we define the ionic radius for any model of O<sup>2-</sup> charge density as the test point which encompasses 99% of the charge cloud,  $r_{99}$ . Using our approach, model functions are derived for  $r_{99}$  ranging from 3.0 to 4.5 au.

Table IV summarizes the charge-density data for O<sup>2-</sup> based on a number of  $r_{99}$ . The shape of the charge cloud ( $\rho_i$ ) can have almost any value, as long as the function is normalized. If the values of  $\rho_i$  are not realistic, the optimization procedure fails to maintain a normalized function.

As a starting point for modeling empirical radii, the closed-shell Hermann-Skillmann charge data are used to describe ions with a variety of  $r_{99}$ . The only changes are the values of  $r_i$  corresponding to the value of  $\rho_i$ . Our procedure obtains models which fit the empirical data with less than a 1% error. The orbital exponents corresponding to these functions are given in Table III.

For the  $r_{99} = 3.5$ , we also explore the variation in the shape of the charge cloud for a fixed radius. The charge density corresponding to fit a drops to "zero" more quickly than the more diffuse fit b.

Using our modeling procedure, analytical functions can be derived for an oxide ion with a variety of shapes and sizes. Our method also provides a test of reasonableness for any numerical or empirical description. The empirical  $\rho_i$  and  $q_{tot,i}$  must give rise to normalized model functions. In optimizing the Slater exponents, the program may create functions which are, in

terms of actual total charge, no longer normalized. This mainly occurs when the optimization procedure modifies exponents in a futile attempt to match unrealistic charge density data. By monitoring the total charge of the atomic system, these erroneous fits can be discarded. The empirical ion data can then be modified until the model function produced by the optimization is normalized.

## BASIS SET DEPENDENCE

Simple basis sets, such as "single- $\zeta$ " (one Slater function describing each orbital), were also investigated using our approach. Models based on these descriptions gave much larger errors than the "Hartree-Fock" basis set. Clearly, one needs a number of orbital functions in order to derive a reasonable fit to arbitrary numerical data. The Hartree-Fock basis set (five Slater-type functions for each shell of electrons) appears to be more than sufficient. The only cases for which a simpler basis set may be useful are studies which focus on the core or tail region of a given ionic charge cloud.

## CONCLUDING REMARKS

A method is presented for fitting numerical atomic charge data with an analytical function. Specifically, a function having the same mathematical form as a Slater-type wavefunction is used to model numerical atomic data. The method is quite straightforward and yields a "wavefunction" which can be used to generate a charge cloud having a specified size and shape. The fitting procedure is illustrated for two types of problems: (1) obtaining analytical models for Hermann-Skillman numerical oxide charge-density data; (2) generating wavefunctions for empirical oxide ions with arbitrary size and charge-cloud shape.

The approach could be easily changed to base the modeling on other functional forms or different charge characteristics of atoms or ions. The optimization of the Slater-type function could also be modified to vary orbital coefficients instead of exponents. Future work will include the incorporation of charge-cloud optimization into the Hartree-Fock atomic SCF method. This refinement would permit the calculation of

normalized self-consistent atomic wavefunctions (and orbital energies) for ions with prescribed electron density characteristics.

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### APPENDIX: COMPLETE ANALYTICAL DESCRIPTION OF THE ATOMIC ORBITALS COMPRISING THE CLEMENTI-ROETTI<sup>2</sup> SLATER-TYPE WAVEFUNCTION

Asymmetric wavefunction: determinant  $|\phi_{1s}\phi_{2s}\phi_{2p}|$ .

General form of the orbitals:  $\phi = \sum c_i \chi_i$ .

#### 1s orbital

$$\phi(1s) = 0.800\chi_1 + 0.049\chi_2 + 0.004\chi_3 + 0.180\chi_4 - 0.001\chi_5$$

#### 2s orbital

$$\phi(2s) = 0.149\chi_1 + 0.029\chi_2 - 0.581\chi_3 + 0.128\chi_4 - 0.536\chi_5$$

#### Slater Functions

$$\chi_1 = \zeta_1^{1/2} e^{-r\zeta_1} Y_{00}(\theta, \phi)$$

$$\chi_2 = \zeta_2^{1/2} e^{-r\zeta_2} Y_{00}(\theta, \phi)$$

$$\chi_3 = \frac{(2\zeta_3)^{3/2}}{[(4)!]^{1/2}} r e^{-r\zeta_3} Y_{00}(\theta, \phi)$$

$$\chi_4 = \frac{(2\zeta_4)^{3/2}}{[(4)!]^{1/2}} r e^{-r\zeta_4} Y_{00}(\theta, \phi)$$

$$\chi_5 = \frac{(2\zeta_5)^{3/2}}{[(4)!]^{1/2}} r e^{-r\zeta_5} Y_{00}(\theta, \phi)$$

#### Spherical Harmonics

$$Y_{00} = 1/[4\pi]^{1/2}$$

#### 2p orbital

$$\phi(2p) = 0.353\chi_6 + 0.203\chi_7 - 0.300\chi_8 + 0.872\chi_9 + 0.003\chi_{10}$$

#### Slater Functions

$$\chi_6 = \frac{(2\zeta_6)^{3/2}}{[4!]^{1/2}} r e^{-r\zeta_6} Y_{10}(\theta, \phi)$$

$$\chi_7 = \frac{(2\zeta_7)^{3/2}}{[4!]^{1/2}} r e^{-r\zeta_7} Y_{10}(\theta, \phi)$$

$$\chi_8 = \frac{(2\zeta_8)^{3/2}}{[4!]^{1/2}} r e^{-r\zeta_8} Y_{10}(\theta, \phi)$$

$$\chi_9 = \frac{(2\zeta_9)^{3/2}}{[4!]^{1/2}} r e^{-r\zeta_9} Y_{10}(\theta, \phi)$$

$$\chi_{10} = \frac{(2\zeta_{10})^{3/2}}{[4!]^{1/2}} r e^{-r\zeta_{10}} Y_{10}(\theta, \phi)$$

#### Spherical Harmonics

$$Y_{10} = (3/4\pi)^{1/2} \cos(\theta)$$

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