

Point-charge electrostatics in disordered alloys

C. Wolverton, Alex Zunger, S. Froyen, and S. -H. Wei
 National Renewable Energy Laboratory, Golden, Colorado 80401
 -Received 17 January 1996; revised manuscript received 21 May 1996!

A simple analytic model of point-ion electrostatics has been previously proposed (R. Magri, S. -H. Wei, and A. Zunger, Phys. Rev. B **42**, 11 388 -1990) in which the magnitude of the net charge q_i on each atom in an ordered or random alloy depends linearly on the number $N_i^{(1)}$ of unlike neighbors in its first coordination shell. Point charges extracted from recent large supercell (256–432 atom) local density approximation (LDA) calculations of $\text{Cu}_{1-2x}\text{Zn}_x$ random alloys now enable an assessment of the physical validity and accuracy of the simple model. We find that this model accurately describes (i) the trends in q_i vs $N_i^{(1)}$, particularly for fcc alloys, (ii) the magnitudes of total electrostatic energies in random alloys, (iii) the relationships between constant-occupation-averaged charges $\langle q_i \rangle$ and Coulomb shifts $\langle V_i \rangle$ -i.e., the average over all sites occupied by either A or B atoms! in the random alloy, and (iv) the linear relation between the site charge q_i and the constant-charge-averaged Coulomb shift \bar{V}_i -i.e., the average over all sites with the same charge! for fcc alloys. However, for bcc alloys the *fluctuations* predicted by the model in the q_i vs V_i relation exceed those found in the LDA supercell calculations. We find that (a) the fluctuations present in the model have a vanishing contribution to the electrostatic energy. (b) Generalizing the model to include a dependence of the charge on the atoms in the first *three (two) shells* in bcc (fcc) — rather than the first shell only — removes the fluctuations, in complete agreement with the LDA data. We also demonstrate an efficient way to extract charge transfer parameters of the generalized model from LDA calculations on small unit cells.

I. INTRODUCTION

The structural stability of alloys and compounds is determined by the kinetic, electrostatic, and exchange-correlation contributions to the total energy. In first-principles calculations based on Hartree-Fock or on density functional theory, the electrostatic portion of the total energy is characterized in terms of the electronic charge density $r(\mathbf{r})$ and the nuclear charges z_i . For systems with uniquely specified nuclear positions $\{\mathbf{R}_i\}$ and charges $\{z_i\}$, the charge density is a well-defined quantity as is the electrostatic (el) portion of the total energy:

$$E_{\text{el}} = \frac{1}{2} \int \int d^3r d^3r' \frac{r(\mathbf{r})r(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \sum_i \left(\int d^3r \frac{r(\mathbf{r})z_i}{|\mathbf{r}-\mathbf{R}_i|} - \frac{1}{2} \sum_{j \neq i} \frac{z_i z_j}{|\mathbf{R}_i - \mathbf{R}_j|} \right) \quad -1!$$

Indeed, in many previous calculations on ordered structures¹⁻⁸ and “supercell” models of random alloys,^{9,10} there are well-defined $\{\mathbf{R}_i; z_i\}$, so the electrostatic energy was obtained from Eq. -1!. However, in simpler approaches,¹¹⁻¹⁵ one approximates the electrostatic energy by replacing the continuous charge density $r(\mathbf{r})$, with fictitious point charges q_i at each site i . For a system with N sites, the electrostatic or Madelung (M) energy is

$$E_M = \frac{1}{2N} \sum_i \left(\sum_{j \neq i} \frac{q_i q_j}{R_{ij}} \right), \quad -2!$$

where R_{ij} is the distance between sites i and j . The Madelung energy may also be written

$$E_M = \frac{1}{2N} \sum_i q_i V_i, \quad -3!$$

where V_i is the Coulomb shift at site i due to all charges other than q_i :

$$V_i = \sum_{j \neq i} \frac{q_j}{R_{ij}}. \quad -4!$$

The point charges are obtained by partitioning $r(\mathbf{r})$ into “domains” (spheres, polyhedra, etc.) and integrating the total charge in each domain. However, because there is not a unique way to partition a three-dimensional space, the point charges are not uniquely defined.

For periodic systems (e.g., ordered structures with a primitive cell or random structures defined by supercells^{5,9-11,16-18}) where all sites i are defined as distinct entities (not as averages) and q_i and \mathbf{R}_i are specified, E_M can be readily computed from Eq. -2! using, for example, the Ewald method. In most statistical approaches to alloys (e.g., the coherent potential approximation, or CPA -Ref. 19! however, one attempts a description of a random alloy without a specification of all *distinct* sites i but rather some averages over

$$\sum_j q_i q_j \neq \sum_j q_i q_j, \quad (6)$$

which leads to a vanishing electrostatic energy for the random alloy,

$$E_M \neq 0, \quad (7)$$

on account of electroneutrality. This approximation (Eq. 6) was based on the expectation that a random -i.e., uncorrelated! distribution of *atoms* on sites would lead to an equally random distribution of *charges*, i.e., the charge on an atom in a given alloy is a property of the atom, irrespective of its environment. Equation 7 has been assumed in many CPA-based calculations¹⁹⁻²⁴ involving the total energy of random alloys. Magri *et al.*¹¹ subsequently criticized this approach as being physically implausible, since the assumption of uncorrelated charges (Eq. 6) means that an *A* atom surrounded locally by only *A* atoms will have the same charge as an *A* atom surrounded by *B* atoms; chemical intuition suggests, however, that the charge on a site will depend on the identity of atoms in its environment because charge transfer is present only between *dissimilar* sites.

Magri *et al.*¹¹ noted that in a random alloy, even though the *occupation* of site *i* is independent of the occupation of other sites by definition, the *charges* on a site do depend on the occupations of other sites. These authors therefore proposed a simple model to describe the magnitude of point charges in disordered -and ordered! alloys: The magnitude of the charge on a site is linearly proportional to the number $N_i^{(1)}$ of unlike nearest neighbors surrounding that site. With this charge model, Magri *et al.* went on to demonstrate that even for the case of a random alloy with completely uncorrelated atomic occupations, charge correlations exist in the alloy and these correlations lead to a nonzero Madelung energy.

Subsequent to the proposal of Magri *et al.*,¹¹ the charge model has been used in many contexts:

-i! Lu *et al.*¹⁰ showed that LDA calculations on ordered compounds produced charge densities which, when integrated inside muffin-tin spheres, gave point charges which reproduced the behavior of the model. They also examined⁵ the effect of the ensuing electrostatic energy of the random alloy on the sign of the ordering energy.

-ii! Abrikosov *et al.*²⁵ and Johnson and Pinski¹³ derived corrections to the CPA total energy which introduced charge correlations in random alloys. These corrections were shown to be consistent with the charge model of Magri *et al.* Several authors subsequently used these corrections in total-energy CPA calculations to determine lattice constants and formation energies of random metallic alloys, finding significant effects due to charge correlations: Johnson and Pinski¹³ estimated the total-energy contribution due to charge correlations to be \geq

where the pseudospin \hat{S}_i is ± 1 if an $A(B)$ atom is located at site i . The set of variables \hat{S}_i for all sites i defines the configuration S . $\hat{S}_{i\gamma k}$ indicates the occupation of the Z lattice sites which are nearest neighbors to i , and hence the summation in Eq. 8 indicates the number of unlike nearest neighbors surrounding the site i . l is a constant which indicates the magnitude of the charge transfer and is an undetermined parameter of the model. Thus, the charge model will give trends in the behavior of physical properties, but will not give numerical values of properties without some input value of l .

Several questions may be asked concerning the parameter l : Should l be explicitly composition dependent? Should l be explicitly volume dependent? Since the equilibrium volume is a function of composition in size-mismatched alloys, an explicit volume dependence of l would lead to an implicit composition dependence. It is important to physically distinguish between these two dependences. Should the values of l be extracted from large-unit-cell or small-unit-cell alloys, i.e., does l contain mostly short-range or long-range information? Values of l have been estimated by LDA calculations,^{10,13,18} ranging from small-unit-cell ordered compounds (~ 8 – 16 atoms), up to large LDA simulations of random alloys (~ 200 – 400 atoms). For computational simplicity, one should know whether it is equally valid to extract values of l from ordered or random alloys, and whether one can even use smaller cells (~ 2 – 4 atoms) than have been currently used.

We next examine the physical consequences of charges which obey Eq. 8. We then compare these consequences with results of LDA supercell calculations in order to assess the physical validity of the model. With regard to the questions raised above, we demonstrate that the simple charge model represents well the charge transfer of *different* unrelaxed configurations at a *common* volume. If more than one volume is considered -e.g., for a lattice-mismatched alloy at more than one composition!, the parameter of the model l would presumably need to be explicitly volume dependent -implicitly composition dependent!. Also, we find that values of l extracted from 2–4-atom LDA calculations agree favorably with those extracted from much larger 200–400-atom LDA calculations, thereby resulting in a drastic computational simplification.

III. PHYSICAL CONSEQUENCES OF THE CHARGE MODEL

A. Average charges

The average charge *on all sites*, \bar{q} is defined as

$$\bar{q} = \frac{1}{N} \sum_i q_i. \quad -9!$$

Combining this with Eq. 8 gives $\bar{q} = 0$, as guaranteed by global charge neutrality. However, what is more interesting is the constant-occupation average \bar{q}_A -or \bar{q}_B), i.e., the average charge of all sites occupied by A (B) atoms. This constant-occupation average is a function of the configuration S and composition x , and we can analytically derive this quantity for any arbitrary configuration. The definition of \bar{q}_A is

$$\bar{q}_A = \frac{1}{N_A} \left(\sum_i q_i \right)$$

atoms on a given sublattice. The extent of LRO in an alloy may be described by one or more LRO parameters h . For example, for an alloy at $x=1/2$ with a single LRO parameter $0 < h < 1$ and no correlations between atoms on the same sublattice, $\bar{P}(h) = h^2 \bar{P}(1)$, so for any state of LRO at $x=1/2$,

$$\langle q_A \rangle = h^2 \langle q_A \rangle_{\text{random}},$$

$$\langle q_B \rangle = h^2 \langle q_B \rangle_{\text{random}},$$

$$D = h^2 D_{\text{random}}. \quad (17)$$

For example, in CsCl ($B2$)-type ordering, $\bar{P}(1) = 1/2$; thus as the degree of LRO increases, D increases due to the increased number of unlike nearest neighbors.

B. Constant-occupation-averaged Coulomb shifts,

$$\langle V \rangle_A \text{ and } \langle V \rangle_B$$

The Coulomb shift V_i (Eq. 4) averaged over all sites $\langle V \rangle$ is zero - just as $\langle q \rangle$ is zero due to global neutrality. A more interesting quantity is the constant-occupation average of the Coulomb shifts on all sites occupied by A atoms in a random alloy,

$$\langle V_A \rangle = \frac{1}{N}$$

and the constant-charge-averaged Coulomb shift $\bar{V}_i(N_i^{(1)})$ -i.e., an average over all sites with the same charge, and hence with the same $N_i^{(1)}$):

$$q_i(N_i^{(1)}) \bar{V}_i(N_i^{(1)}), \quad -25!$$

where g (in Ry²¹) is the slope of this linear relation,

$$g_{\text{fcc}}(x \approx 1/2) \approx 0.132R_1,$$

$$g_{\text{bcc}}(x \approx 1/2) \approx 0.163R_1. \quad -26!$$

Note that \bar{V}_i is a constant-charge average -still leaving the $N_i^{(1)}$ dependence!, in contrast to the constant-occupation averaged \bar{V}_i . To evaluate the *fluctuations* in $V_i(N_i^{(1)})$ about \bar{V}_i , we perform large-unit-cell simulations for a single, randomly selected configuration. Equal numbers of atomic types A and B ($x \approx 1/2$) are distributed at random over the 256 fcc sites and 432 bcc sites of the simulation cell. Point charges q_i are then assigned by the model of Eq. -8!. Using the Ewald method, we then calculate the Coulomb shifts V_i @Eq.

$1.414R_1$, and $1.732R_1$ for $n=1,2,3$, while for bcc these distances are R

(20.12560.002), while for bcc alloys, the slope of the model (20.163) is too large in magnitude relative to the LDA result (20.11560.001).

The relationship between q_i and the distinct Coulomb shift V_i (not the constant-charge-averaged \bar{V}_i) as obtained in the simple model of Eq. 8 is shown in Fig. 2, where it is contrasted with the results of the LDA calculations of Ref. 18. The fluctuations in Coulomb shift about the average linear behavior of q_i and V_i are quite small in the fcc random alloy, but are substantial in the bcc alloy. We have next determined the effect of these fluctuations on the electrostatic energy E_{MR} of the random alloy: If the linear relation Eq. 25 between charge and Coulomb shift (neglecting

fluctuations) is used in Eq. 3 to compute the random alloy energy, we recover precisely the same energy *including fluctuations* derived in Eq. 24. Thus, although the fluctuations in V_i are graphically impressive (Fig. 2), *the energetic consequence of these fluctuations is strictly zero*, simply indicating that the fluctuations in Coulomb shift are symmetrical about the average linear behavior.

D. Charge-charge correlations functions

The simple charge model predicts specific values for the

correlations are a bit unclear: In Ref. 18, the authors note that for 256-atom LDA supercell calculations, the nearest-neighbor correlations are sizeable, but they also note that the values beyond the nearest-neighbor shell are smaller than the predictions of the model, although these values are not too well known due to the relatively small size of the simulation cell. When larger LDA supercell simulations become available, a comparison of charge-charge correlations from LDA supercell with the predictions of Eq. -23! -and those of the generalized charge model described below! would be of interest. The analytic values of the charge-charge correlation functions of Eq. -23! are plotted in Fig. 3. We have also compared these analytic values with those obtained from our large-unit-cell simulations of the charge model -not shown!. Although the correlations for the nearest-neighbor shell are robust with respect to unit cell size, the correlations for the more distant third, fourth, fifth shells are extremely sensitive to the size of the simulation cell: For a single fcc 256-atom simulation, one can even find third- and fourth-neighbor correlations which have an opposite sign relative to the exact analytic values. Even for very large -16 384-atom! fcc simulations configurationally averaged over 20 configurations, the third- and fourth-neighbor correlations may differ from the analytic values by $\sim 10\%$. Thus, in order to compare the LDA charge-charge correlations for random alloys with the analytic results of the simple charge model, the size of the LDA supercell calculations would have to be significantly increased.

E. Coulomb energy of random alloys

The Madelung energy of the simple charge model for a random alloy is given in Eq. -24! in terms of the parameter l and the nearest-neighbor distance R_1 . If we use the numerical values for l given in Eq. -28! and the nearest-neighbor distances used in the LDA supercell calculations for Cu-Zn alloys,

$$R_1^{\text{fcc}} \approx 4.879 \text{ a.u.}; \quad R_1^{\text{bcc}} \approx 4.763 \text{ a.u.}, \quad -30!$$

we obtain the electrostatic energies of the simple charge model for Cu-Zn:

$$^{\wedge}E_{M\&R}^{\text{fcc};x} \approx 22.60 \text{ mRy/atom},$$

$$^{\wedge}E_{M\&R}^{\text{fcc};x} \approx 22.18 \text{ mRy/atom},$$

$$^{\wedge}E_{M\&R}^{\text{bcc};x} \approx 22.57 \text{ mRy/atom}. \quad -31!$$

These values are compared with the Cu-Zn LDA supercell values¹⁸ in Table I:

$$^{\wedge}E_{M\&R}^{\text{fcc};x}$$

-iv! The Coulomb energies of the model are extremely accurate with respect to the LDA values -to within 0.1 mRy/atom!.

-v! The slope of the $q \geq V$ relation, g , in Fig. 2 is the same for A and B . The LDA supercell calculations also show similar slopes (g/R_1) for charges on Cu (20.123) or Zn (20.127) atoms in the fcc $x51/2$ alloy, or for Cu (20.114) or Zn (20.116) atoms in the bcc $x51/2$ alloy.

-vi! The slope of the charge *versus* number of unlike nearest neighbors -Fig. 1! are negatives of one another. LDA supercell calculations -for fcc alloys! support this -Fig. 1!.

-vii! In the impurity limit, the model predicts that the charge on A embedded in pure B is equal -in magnitude! to that of B embedded in pure A ,²⁸

$$\hat{q}_A \sim x \quad \hat{q}_B \sim -x \quad (33)$$

The LDA supercell calculations also show this behavior -see Fig. 1! for an atom surrounded completely by unlike neighbors. Note that neither the simple model nor the LDA supercell simulations include the effects of atomic relaxations, which could likely eliminate the degeneracy of Eq. -33!. To describe relaxed configurations, it is anticipated that more parameters -e.g., bond lengths! would need to be introduced into the model.#

-viii! l is composition independent in the charge model; values of l -Table I of Ref. 18! extracted from the LDA supercell calculations also demonstrate that l is not sensitive to concentration. We reiterate that the charge model describes only unrelaxed configurations at a fixed volume. For lattice-mismatched systems, alloys of different composition will have different volumes, and the charge transfer will depend on this volume. To model this effect, l should be explicitly volume dependent. This *explicit* volume dependence would lead to an *implicit* dependence of l on composition. -Presumably, this implicit composition dependence is not seen in the LDA supercell data of Ref. 18 due to the fact that the system studied, Cu-Zn, has a relatively small lattice mismatch.! However, this should not be confused with an *explicit* composition dependence of l .

Although there are many cases of agreement between the predictions of the charge model @Eq. -8!# and the electrostatics of large LDA calculations, certain discrepancies arise in these comparisons:

-i! The LDA calculations show that the charge is not a single-valued function when plotted versus the number of unlike nearest neighbors -Fig. 1!. Although there is not much width to the distribution for fcc alloys, there is a significant width for bcc alloys. Also demonstrated by Fig. 1 is that charges in the model of Eq. -8! are quantized since the number of unlike nearest neighbors must be an integer. The LDA calculations -particularly for bcc! show no such quantization.

-ii! The slope of the $q \geq V$ relation (g/R_1) for bcc alloys -Table II! is significantly larger in magnitude in the model

tions. The fcc model for nearest neighbors only is already accurate with respect to LDA calculations (Figs. 1 and 2), thus generalizing the fcc charge model to first and second neighbors does not produce a large effect. In Fig. 6, we show the values of the parameters l_s versus distance of the shell s . One can see that the parameters are reasonably well fit by an exponential function,

$$l_s \approx \frac{l_1 R_1}{R_s} e^{-R_s / R_0}, \quad (37)$$

with a decay length of $R_0 \approx 0.34 R_1$. This suggests that in an alloy the net charge on each site is screened effectively in a very short range.

Since the generalized charge model predicts a linear $q \approx V$ relation in disordered alloys, with almost no fluctua-

current LDA supercells, we note that the generalized charge model changes the sign of the second-neighbor correlation in both fcc and bcc relative to the simple model. It would be interesting to compare these correlations with those of LDA when larger supercell calculations become available.

The charge q_i versus the generalized number of neighbors \tilde{N} is shown in Fig. 4 for LDA and for the model of Eq. (34). For fcc alloys, the corrections induced by generalizing the charge model are small since the original model of Eq. (8) is already very good. The predictions of the generalized charge model fit the LDA supercell data extremely well even for bcc alloys, where the nearest-neighbor model of Eq. (8) was lacking.

Figure 5 shows the relation between charge q_i and Coulomb shift V_i of the generalized charge model, comparing the results with LDA. Like LDA, the generalized charge model predicts a linear relation between q_i and V_i with almost no fluctuations. Furthermore, the slope of these linear relations are in excellent agreement with the LDA supercell data (Table II), provided that cutoffs for fcc and bcc are at second- and third-neighbor shells, respectively. Thus, the generalized charge model of Eq. (34) rectifies all of the discrepancies noted above (Sec. V A) between model and LDA calcula-

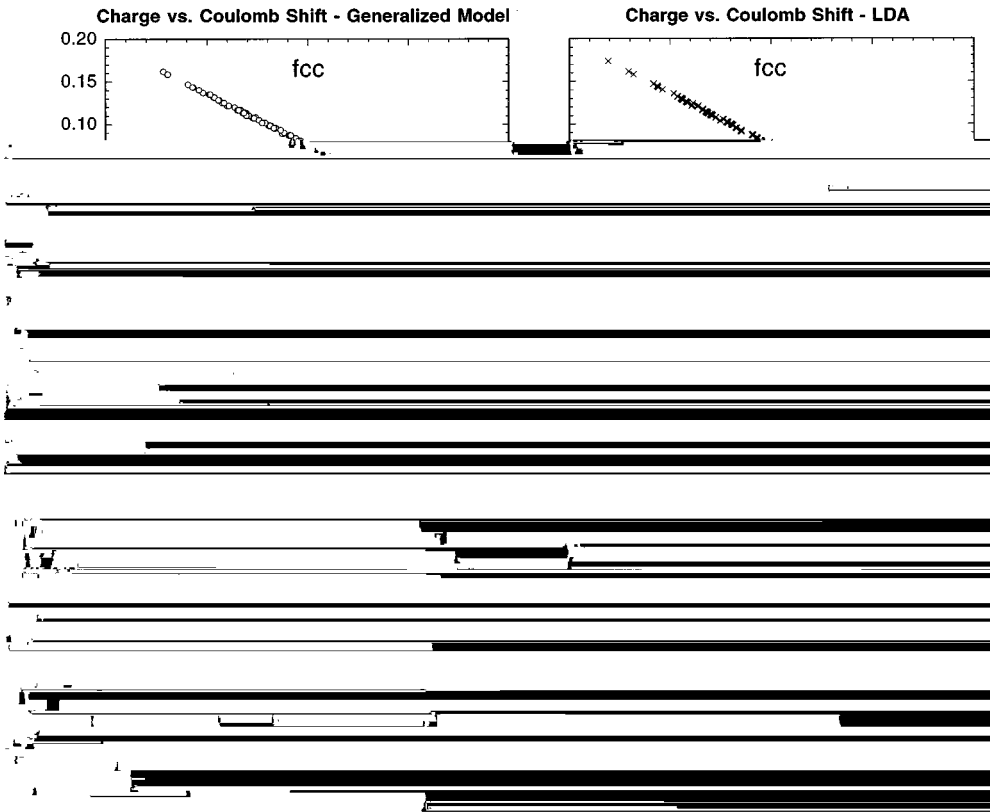


FIG. 5. Charge versus Coulomb shift as predicted by the generalized charge model of Eq. -34! using the values of l_s and R_1 given in Eqs. -36! and -30!.

The LAPW charges for the six small-unit-cell compounds calculated were fit to a form of the generalized charge model of Eq. -34! with first-third neighbor shells. The parameters of the generalized model fit to these small-unit-cell calculations,

$$l_1^{bcc} \approx 0.00680, \quad l_2^{bcc}/l_1^{bcc} \approx 0.609, \quad l_3^{bcc}/l_1^{bcc} \approx 0.131, \quad -39!$$

agree well with those fit to large-unit-cell data @Eq. -36!#. The parameters of Eq. -39! fit to small-unit-cell LDA calculations lead to a $q \approx V$ relation which is linear, with no fluctuations,

and has a slope of $g/R_1 \approx 0.112$, compared with $g/R_1 \approx 0.119$ for the parameters of the generalized model fit to large-unit-cell LDA data. The charges extracted from small-unit-cell LDA calculations are shown in Fig. 7 as a function of generalized number of neighbors \tilde{N} using the values of l_s in Eq. -39!#. These calculations demonstrate that the parameters of the generalized model may be determined from calculations of several small-unit-cell ordered compounds in unrelaxed geometries at fixed volume. If one

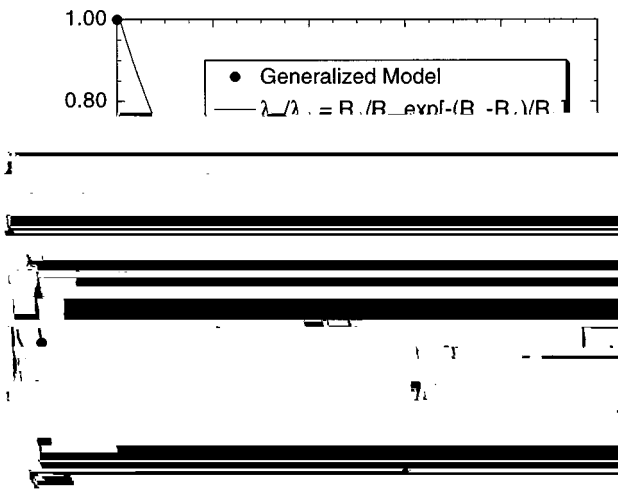


FIG. 6. Charge transfer parameters l_s of generalized model of Eq. -34! as a function of distance. Also shown is a fit to the parameters to the exponential function of Eq. -37!. The fitted value is R_0

wishes to assess the explicit volume dependence of the parameters, one only needs to repeat these types of calculations at a few different volumes. We have performed such volume-dependent calculations at $a = 0.0536$ and $a = 0.0575$ -in addition to the $a = 0.0556$ calculations described above

$$r_{n,l}^{B-1!} \int_l^{\tilde{Z}} \frac{1}{2^{Z_1 2 K_1 2 l}} \frac{\int_{Z_1 2 M}^K \int_{K_1 2 K}^{M 2 l}}{\int_{Z_1 2 l}^{K_1}}, \quad -A8!$$

where $K_1 2 l 2 1$ and the following inequalities must be satisfied:

$$1 < n < Z_1,$$

$$0 < l < n 2 1; \quad l < \tilde{Z},$$

$$0 < n 2 1 2 l < K_1,$$

$$n 2 1 2 l < Z_1 2 M,$$

$$K_1 2 - n 2 1 2 l < M 2 1. \quad -A9!$$

Combining Eqs. -44!-48!, we have

$$q_1 - M! 5 - Z_1 2 M! \left(\prod_{n=0}^{Z_1 2 1} 2 2 n! \right) \left(\prod_{l=0}^n r_{n,l}^{A-1!} \right) \\ 1 M \left(\prod_{n=1}^{Z_1} 2 n! \right) \left(\prod_{l=0}^{n 2 1} r_{n,l}^{B-1!} \right), \quad -A10!$$

where $r_{n,l}^{A(1)}$ and $r_{n,l}^{B(1)}$ are subject to the constraints -A7! and -A9!.

More distant-neighbor shells: For $m = 1$,

$$q_m - M! 5 \frac{Z_m}{2} @ q_m^A 1 q$$

$$B: \int_{\frac{1}{2}}^1, 2 \frac{1}{2}, 2 \frac{1}{2} \Big| a,$$

$$A: \int_1, 2 \frac{1}{2}, 2 \frac{1}{2} \Big| a,$$

$$B: -1, 2 \frac{1}{2}, 0 \Big| a,$$

$$A: \int_{\frac{3}{2}}^3, 2 \frac{1}{2}, \frac{1}{2} \Big| a,$$

$$A: \int_{\frac{1}{2}}^1, 0, 2 \frac{1}{2} \Big| a,$$

$$B: \int_{\frac{1}{2}}^1, 2 \frac{1}{2}, 0 \Big| a,$$

$$B: \int_1, 2 \frac{1}{2}, 1$$