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## Pauli-Force Model Potential for Solids\*

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A model potential previously applied to molecules is adapted to the study of structural trends in solids. The potential, which has simple analytic one-electron eigenfunctions and eigenvalues, is based upon a Pauli-force concept and retains the salient features of *ab initio* pseudopotentials. The eigenvalues are of the quantum-defect form, so that treatment of the energy dependence of the potential parameter is particularly straightforward. A form factor is calculated in a local-screening approximation, and algebraic expressions for a core radius  $r_c$  and the form-factor node  $q_0$  are obtained. These expressions have transparent physical interpretations, and form the basis for a discussion of chemical trends in  $r_c$  and  $q_0$  in terms of a few simple parameters. The connection with well-known local model potentials is briefly explored.

### I. INTRODUCTION

During the past few years, the pseudopotential theory of solids has reached chemical fruition in the systematic treatments of covalency by Phillips<sup>1</sup> and of metallic cohesion and structure by Heine and co-workers.<sup>2-4</sup> Progress in the application of the method to molecules has been less rapid. Recently, however, one of us has shown<sup>5</sup> that certain trends in molecular structures are described by a simple model potential which may be understood in terms of a "Pauli force" between core and valence electrons. The potential has analytic one-electron eigenfunctions and eigenvalues, and leads naturally to useful constructs such as orbital electronegativities and comparative hybridizations.

In this paper we establish a basis for interpreting structural trends in solids in terms of this same model potential. In adding yet another model potential to the assortment already available, we are

not primarily concerned with matching the accuracy of successful calculations already in the literature; rather, we seek chemical insight into their results. From this point of view, the choice of a potential having analytic eigenfunctions and eigenvalues is especially attractive in that it circumvents much of the mathematics associated with the usual model potentials. In particular, the connection between potential parameters and atomic spectral data is algebraic, and in terms of these parameters we are able to develop simple expressions for structurally important quantities normally accessible only to numerical calculation. These new expressions lend themselves to straightforward physical interpretation. Insofar as the physical basis of our potential is different from others, such interpretation offers alternative descriptions of structural trends, and in some cases may elucidate their chemical nature more clearly. Moreover, the use of a potential which has already been ap-

plied to molecules offers the prospect of interrelating structural trends in molecules and solids, with the aim of understanding both in terms of trends in a single set of atomic properties.

## II. PAULI-FORCE MODEL POTENTIAL

### A. General Considerations

*Ab initio* pseudopotentials for various atoms have been determined by Szasz and McGinn<sup>6</sup> and by Kahn and Goddard.<sup>7</sup> These potentials are nonlocal operators which may be written as

$$V(r) = \sum_l V_l(r) \phi_l, \quad (1)$$

where  $\phi_l$  is the projection operator over the subspace of spherical harmonics of angular momentum quantum number  $l$ . In general, the  $l$ -dependent functions  $V_l(r)$  exhibit the following properties: (a) At large distances  $r$ , the dominant term in  $V_l(r)$  behaves as  $-Z/r$ , where  $Z$  is the net charge of the core system. (b) If the core contains orbitals of a given  $l$ , then  $V_l(r)$  possesses a local minimum at an  $r$  corresponding to a core radius. Inside this radius there is a large positive potential barrier, beyond which  $V_l(r)$  falls to negative infinity at very small  $r$ . (c) If the core does not contain orbitals of a given  $l$ , there is no potential barrier and  $V_l(r)$  approaches negative infinity without a local minimum.<sup>8</sup>

Unfortunately, the *ab initio* pseudopotentials are numerically unwieldy and difficult to use either in large calculations or in interpretative studies. We therefore seek a model potential which retains the salient physical features of these pseudopotentials, but avoids their mathematical complexity.

We begin by recalling that empirically, the valence energy spectrum of a monovalent atom is well represented by the quantum-defect formula<sup>9</sup>

$$E = -C/[n + \Delta(l)]^2, \quad (2)$$

where  $C$  is a constant,  $n$  is the principal quantum number, and the quantum defect  $\Delta$  is a function of  $l$ . It is natural to surmise that a model potential whose eigenvalues are of the form (2) and which has the above properties (a)–(c) might be a good approximation to the atomic pseudopotential. This is, in fact, the case. The model potential

$$V(r) = -\frac{Z}{r} + \sum_l \frac{B_l \phi_l}{r^2}, \quad (3)$$

which has been successfully applied to both atoms<sup>10</sup> and molecules,<sup>5,11</sup> has analytic eigenfunctions with eigenvalues of the form (2). The dominant long-range term in the potential is clearly  $-Z/r$ , as in (a). For  $B_l$  positive, the model potential possesses a large positive barrier at small  $r$ , as in (b); the failure to approach negative infinity at very small  $r$  is chemically unimportant, as there is

little valence-orbital density near the origin.<sup>12</sup> If  $B_l$  is negative, there is no barrier in the potential, as in (c).

The general features of this model potential (as well as those of the *ab initio* potentials) may be simply understood. Where there are core orbitals having the  $l$  quantum number under consideration, the pseudopotential replaces the core-valence-orthogonality requirement by a repulsive Pauli force which acts to keep valence electrons out of the core region. The Pauli force leads to a positive  $B_l$  and a potential barrier. In case (c), however, the core and valence orbitals are already orthogonal. Here the dominant effect is the polarization of the core system by the valence electrons, which creates a charge-induced dipole interaction. The resulting negative values of  $B_l$  can be interpreted in terms of an effective core dipole, and indeed can be estimated from core polarizabilities.<sup>10</sup>

### B. Core Radius and Cancellation Theorem

Before proceeding further, we note that the model potentials commonly applied to solids are rather different from the *ab initio* pseudopotentials and from the model potential presented here. Specifically, inside some effective core radius the conventional model potentials are set equal either to zero (the “empty-core” model of Ashcroft<sup>13</sup>) or to a small  $l$ -dependent constant (the Heine–Abarenkov model potential<sup>14</sup>). A primary motivation for such a choice lies in the cancellation theorem, which in its simplest form states that for functions which are smooth<sup>15</sup> on the scale of the core radius, the matrix elements of the pseudopotential evaluated over core space are small.<sup>2</sup> If we approximate the smooth wave functions by constants in the core region, the theorem requires that

$$\langle V \rangle_{r_c} = \int_0^{2\pi} \int_0^\pi \int_0^{r_c} V(r) r^2 dr \sin\theta d\theta d\phi \approx 0. \quad (4)$$

Clearly, if  $V(r)$  is zero or small in core space, the cancellation theorem is satisfied. We emphasize, however, that this is not a necessary requirement: if  $V(r)$  has regions of both negative and positive sign,  $\langle V \rangle_{r_c}$  may be small regardless of the magnitude of  $V(r)$  at a given point.

To illustrate, we evaluate the integral in (4) for a local form of our model potential,

$$V^{loc}(r) = -Z/r + B/r^2. \quad (5)$$

We take the core radius to be the classical stationary point at which the repulsive Pauli force is equal to the nuclear attractive force—that is, the minimum in  $V^{loc}(r)$ . Thus

$$r_c^{loc} = 2B/Z \quad (6)$$

and

$$\langle V \rangle_{r_c} = 4\pi(-\frac{1}{2}Zr_c^2 + Br_c) = 0. \quad (7)$$

If smooth functions are used in (4) instead of constants,  $\langle V \rangle_{r_c}$  is no longer identically zero, but is in general still small. Thus the model potential employed here, while not motivated by the cancellation theorem, does satisfy it formally, and has the additional advantages of resembling the *ab initio* pseudopotentials, possessing analytic eigenfunctions and eigenvalues, and yielding a core radius as the natural consequence of a balance of forces.

### C. Radial $l$ Numbers

The analytic eigenvalues of the Pauli-force model potential constitute algebraic relations between experimental atomic-term values and the potential parameters  $B_l$ . In this section we cast these relations in a particularly simple form, and demonstrate that, in principle, the problem of evaluating these parameters at energies appropriate to solids adds no important complications.

If the  $B_l$ 's are rewritten as<sup>5,16</sup>

$$B_l = \frac{1}{2}[l'(l'+1) - l(l+1)], \quad (8)$$

where  $l' = l'(l)$ , then the radial Schrödinger equation is of hydrogenic form with  $l$  replaced by  $l'$ . The eigenvalues

$$E(n, l, l', Z) = -Z^2/2(n+l'-l)^2 \quad (9)$$

are of the quantum-defect form (2) with  $\Delta = l' - l$ . In this formulation, all information regarding core effects on the valence system is contained in the charge  $Z$  and the "radial  $l$  numbers"  $l'$ . The radial  $l$  numbers, in turn, are antecedent to traditional constructs such as hybridization, orbital electronegativity, and core radius.<sup>5</sup>

Inasmuch as they are determined directly from atomic spectral data according to the simple algebraic formula (9), the genesis of the  $l'$ 's in atomic structure is transparent. In this respect, the Pauli-force model potential offers certain computational and conceptual advantages over the Heine-Abarenkov potential,<sup>14</sup> whose corresponding parameters  $A_l$  are available from experimental data only through auxiliary numerical procedures for matching wave functions at a core radius.

Now it is well known that the quantum defect  $\Delta(l)$  is a function of the energy, so that (9) becomes exact only if we write

$$l' = l'(l, E). \quad (10)$$

Then if the potential (3) is to be applied accurately to solids, it is necessary to evaluate the  $l'$ 's at the Fermi energy  $E_F$ <sup>17</sup>; we designate the result as

$$\hat{l}(l) \equiv l'(l, E_F), \quad (11)$$

and denote the corresponding value of  $B_l$  as  $\hat{B}_l$ .

We now argue that  $l'(l, E)$  is a smooth function of the energy which can, in principle, be extrapolated from the ionic-term values (9) to obtain  $\hat{l}(l)$ .

When (3) and (8) are employed in the radial Schrödinger equation, the solution, regular at the origin, is<sup>10</sup>

$$R_{p, l'}(r) = C(p, l') r^{l'} e^{-\gamma r} F(1-p | 2l'+2 | 2\gamma r), \quad (12)$$

where  $C$  is a constant,  $F$  is the confluent hypergeometric function of the first kind,  $p = Z(2E)^{-1/2} - l'$ , and  $\gamma = Z/(p+l')$ . At the eigenvalues (9),  $p = n - l$ , and  $R_{p, l'}(r)$  can be regarded as a hydrogenic radial function  $R_{p, l}(r)$  with integral  $p$  but with nonintegral  $l$ . This is to be contrasted with the usual quantum-defect formulation<sup>18</sup> (appropriate, for example, to the Heine-Abarenkov model potential<sup>14,19,20</sup>), where the experimental quantum defect is manifested at eigenvalues as a nonintegral  $p$  with integral  $l$ . In an expression such as (9), the distinction is, of course, merely formal, but the same is not true for the wave function (12). The transfer of the quantum defect from the first to the second index of the confluent hypergeometric function has important consequences for the behavior of the defect as a function of energy. If (12) and its derivatives are to be bounded for finite  $r$  and regular at the origin,  $l'(E)$  must remain analytic and can never cross a negative integer. Moreover, it is immediately clear from inspection of (12) that  $l'(E)$  has no "forced zeros" or rapid oscillations in the sense discussed by Ham.<sup>18</sup> As a consequence, unlike the usual representation of experimental quantum defect,<sup>18-20</sup>  $l'(E)$  is a smooth function of the energy, which can be plotted and extrapolated directly from the term values (9). For energies at and below the lowest valence eigenvalue  $p = 1$ , the resulting radial wave functions (12) are nodeless (except at the origin); at all valence energies they are "smooth" in the sense of Sec. II B.

### III. STRUCTURAL PARAMETERS AND CHEMICAL TRENDS

Having established a physical and mathematical basis for the application of the Pauli-force model potential to solids, we are in a position to undertake a full calculation of the nonlocal form factor, and to apply the results to structural calculations in the usual manner.<sup>4</sup> Preliminary work<sup>21</sup> indicates that, at least in the region  $q < 2k_F$ , form factors comparable to those of Animalu and Heine<sup>17</sup> and of Shaw<sup>19</sup> are available at a substantial saving of computational effort.

In this paper, however, we eschew the full calculation in favor of a series of approximations designed to retain the physical transparency of the Pauli-force model potential. These are not necessarily adequate for detailed calculations of the form factor, but we shall find them quite sufficient,

so long as we limit our attention to a few important structural parameters. Inasmuch as the role of these parameters in determining structure is, for the most part, well established,<sup>4</sup> we obtain by this "back-of-the-envelope" approach a set of simple expressions which directly relate chemical trends in solids to trends in atomic structure.

#### A. Form Factor $V(q)$

To begin, we express the screened Fermi-surface form factor  $V(q)$  in the approximation that the dielectric screening is regarded as local. For our present purposes, we find it sufficiently accurate to write

$$V(\vec{q}, \vec{k}) = \langle \vec{k} + \vec{q} | V | \vec{k} \rangle / \epsilon(q), \quad (13)$$

where  $\epsilon(q)$  is the usual Lindhard dielectric function modified to account for exchange and correlation.<sup>22</sup> After expansion of  $e^{i\vec{k}\cdot\vec{r}}$  in spherical harmonics, the matrix element of the Pauli-force model potential in (13) is

$$\Omega \langle \vec{k} + \vec{q} | V | \vec{k} \rangle = -\frac{4\pi Z}{q^2} + 4\pi \sum_l (2l+1) \hat{B}_l P_l(\cos \theta_{\vec{k}, \vec{k}+\vec{q}}) \times \int_0^\infty j_l(|\vec{k} + \vec{q}|r) j_l(kr) dr, \quad (14)$$

where  $\Omega$  is the volume of a unit cell, and  $P_l$  and  $j_l$  represent Legendre polynomials and spherical Bessel functions, respectively. By converting to ordinary Bessel functions and applying a theorem given by Watson,<sup>23</sup> we obtain

$$V(\vec{q}, \vec{k}) = -\frac{4\pi Z}{\Omega q^2 \epsilon(q)} + 2\pi^2 \sum_l \hat{B}_l \frac{P_l(\cos \theta_{\vec{k}, \vec{k}+\vec{q}}) (k_\zeta/k_\zeta)^{l+1/2}}{\Omega \epsilon(q) (k_\zeta k_\zeta)^{l+1/2}}. \quad (15)$$

Here  $k_\zeta$  is the lesser of  $|\vec{k} + \vec{q}|$  and  $|\vec{k}|$ , while  $k_\zeta$  is the greater.

If we confine our attention to scattering on the Fermi sphere, so that

$$\begin{aligned} |\vec{k}| &= |\vec{k} + \vec{q}| = k_F, & q < 2k_F \\ |\vec{k}| &= k_F, \quad |\vec{k}| - \vec{q}, & q > 2k_F \end{aligned} \quad (16)$$

then (15) is reduced to

$$V(q) = \left[ \frac{-4\pi Z}{q^2} + \frac{2\pi^2}{k_F} \sum_l \hat{B}_l P_l \left( 1 - \frac{q^2}{2k_F^2} \right) \right] / \Omega \epsilon(q), \quad q < 2k_F \quad (17a)$$

$$= \left[ \frac{-4\pi Z}{q^2} + \frac{2\pi^2}{q - k_F} \sum_l \hat{B}_l \left( \frac{-k_F}{q - k_F} \right)^l \right] / \Omega \epsilon(q), \quad q > 2k_F. \quad (17b)$$

For  $q < 2k_F$  the form factors (17a) are usually in good agreement with those calculated by Animalu and Heine<sup>17</sup> from their model potential based upon

the cancellation theorem. For large  $q$ , however, the region of real space close to the nucleus—where our model potential does not always behave like the *ab initio* pseudopotentials—is emphasized, and the convergence of (17b) to zero as  $q \rightarrow \infty$  is comparatively slow. We have already remarked that bonding in real space is dominated by regions of high-valence electron density, away from the nucleus; in reciprocal space this corresponds to the familiar observation that structural trends are determined largely by the behavior of  $V(q)$  in the region  $q < 2k_F$ . We therefore expect (17) to render structural and chemical information faithfully, but to be of doubtful value for computing phonon spectra or other properties sensitive to the high- $q$  behavior of the form factor. Presumably the latter situation could be improved by inclusion of a damping factor in (17b), but we have not pursued the point. We are concerned here not with the utility of (17b), but with the chemistry and physics implicit in (17a).

#### B. Algebraic Expression for $q_0$

It is well known that the gross shapes of  $V(q)$  for diverse elements are remarkably similar<sup>3,4</sup>; the function is negative for small  $q$ , usually crosses the axis at a point  $q_0$ , passes through a maximum, and is damped for large  $q$ . The structural significance of the node  $q_0$  has been extensively documented<sup>4,24</sup>; chemically, it is undoubtedly the most important single parameter describing the form factor.<sup>4</sup> From (17a),  $q_0$  is given (in atomic units) by

$$q_0 = \left( \frac{2Zk_F}{\pi \sum_l \hat{B}_l P_l (1 - q_0^2/2k_F^2)} \right)^{1/2}. \quad (18)$$

Equation (18) can usually be solved exactly, but we find it more instructive to simplify the expression slightly. We recall that although  $q_0$  itself varies considerably among the elements,  $q_0/2k_F$  remains very nearly constant. In fact, Heine and co-workers<sup>4</sup> have found that for some 23 elements, the average value of  $q_0/2k_F$  is

$$\langle q_0/2k_F \rangle_{av} = 0.82, \quad (19)$$

with a standard deviation of only 0.05. To be sure, these deviations do contain basic chemistry<sup>4,24</sup> and are often of central importance in determining structure, but (19) remains sufficiently accurate that little is lost by substituting it into the arguments of the Legendre polynomials of (18):

$$q_0 \approx \left( \frac{2Zk_F}{\pi \sum_l \hat{B}_l P_l (-0.345)} \right)^{1/2}. \quad (20)$$

We are now ready to calculate  $q_0$ , given reliable values of  $\hat{B}_l$ . In Sec. IIC we remarked that  $l'(E)$  is a slowly varying function of the energy which can, in principle, be extrapolated to the Fermi

TABLE I. Approximate  $\hat{l}$  parameters for solids.<sup>a</sup>

	Elements	$\hat{l}(0)$	$\hat{l}(1)$	$\hat{l}(2)$
Z=1	Li	0.588	1	2
	Na	0.627	1.117	2
	K	0.770	1.234	1.854
	Rb	0.805	1.288	1.767
	Cs	0.869	1.351	1.552
Z=2	Be	0.729	1	2
	Mg	0.906	1.265	2
	Zn	0.740	1.140	2
	Cd	0.794	1.199	2
	Hg	0.703	1.157	2
	Ca	1.141	1.497	1.313
	Sr	1.221	1.604	1.432
	Ba	1.332	1.721	1.414
Z=3	B	0.797	1	2
	Al	1.075	1.371	2
	Ga	1.011	1.333	2
	In	1.090	1.439	2
	Tl	1.026	1.435	2
Z=4	C	0.837	1	2
	Si	1.196	1.450	2
	Ge	1.182	1.480	2
	Sn	1.312	1.626	2
	Pb	1.268	1.644	2
Z=5	P	1.287	1.510	2
	As	1.330	1.602	2
	Sb	1.471	1.754	2
	Bi	1.464	1.819	2
Z=6	S	1.358	1.559	2
	Se	1.448	1.699	2
	Te	1.602	1.862	2

<sup>a</sup>Calculated as described in the Appendix.

energy. In the present simplified context, however, we dispense entirely with this intermediate step in the analysis, and instead present in the Appendix a scheme for estimating  $\hat{l}(l)$  by inspection, directly from atomic spectral data. The approximations involved are not, in general, serious, and are so chosen that the errors they do introduce tend to compensate for the inaccuracy of replacing (18) with (20). The results for 30 elements are listed in Table I.

Values of  $q_0$  calculated from (20), (8), and Table I are compared to accepted values in Table II. Our results agree closely with the values determined from the Heine–Abarenkov model potential<sup>14,17</sup> and with those obtained by fits to experimental data.<sup>3</sup> The results for elements which do not possess low-lying  $d$  states generally agree to within a few percent; both the new and the old  $q_0$ 's for the remaining elements are less certain.

### C. Trends in $q_0$

The variation of  $q_0$  through the Periodic Table becomes more transparent if the approximation (19)

is again employed in (20) to obtain

$$q_0 \approx \frac{2.44Z}{\sum_l \hat{B}_l P_l(-0.345)} \quad (21)$$

Inasmuch as it is approximately proportional to the attractive term of the model potential divided by the repulsive term,  $q_0$  may be regarded as a "balance point" between the attractive Coulomb force and the repulsive Pauli force. As before, the Legendre polynomials are weighting functions which determine the contribution of each  $l$  component.

Table II shows that  $q_0$  increases dramatically across a row of the Periodic Table. According to (21), this is due to the large increase in core charge; this increase is far more important than any change in the repulsive term.

Within a column of the Periodic Table,  $q_0$  de-

TABLE II. Values of  $q_0$ .

Elements	$k_F$ <sup>a</sup>	$q_0$ [Eq. (27)]	$q_0$ (accepted) <sup>b</sup>
Li	0.5890	0.90	0.91
Na	0.4882	0.83	0.87 (0.97)
K	0.3947	0.61	
Rb	0.3693	0.56	
Cs	0.3412	0.48	
Be	1.0287	1.44	1.44
Mg	0.7242	1.14	1.13 (1.13)
Zn	0.8342	1.37	1.42 (1.42)
Cd	0.7423	1.25	1.28 (1.28)
Hg	0.7213	1.34	1.27 (1.33)
Ca	0.5865	0.73	0.79 <sup>c</sup>
Sr	0.5380	0.70	0.75 <sup>c</sup>
Ba	0.5188	0.66	0.64 <sup>c</sup>
B	1.2177	1.80	1.87
Al	0.9276	1.40	1.35 (1.39)
Ga	0.8776	1.43	1.40 (1.49)
In	0.7972	1.32	1.32 (1.43)
Tl	0.7738	1.37	1.39
C	1.4594	2.20	2.25
Si	0.9590	1.53	1.50 (1.53)
Ge	0.9206	1.53	1.53 (1.60)
Sn	0.8674	1.40	1.42 (1.46)
Pb	0.6350	1.43	1.47 (1.50)
P	1.0008	1.66	1.64 (1.68)
As	1.0065	1.65	1.63 (1.65)
Sb	0.8986	1.47	1.48 (1.57)
Bi	0.8520	1.43	1.47 (1.50)
S	1.0158	1.76	(1.77)
Se	0.9927	1.69	1.67 (1.75)
Te	0.9209	1.53	1.53 (1.64)

<sup>a</sup>From Ref. 3.

<sup>b</sup>From Ref. 3 unless noted otherwise. Where two entries appear, the first is from the form factors of Ref. 17, while the value in parentheses was obtained by fits to experimental data.

<sup>c</sup>From A. O. E. Animalu, Proc. Roy. Soc. Lond. **294**, 376 (1966).

creases from the first- to the second-row elements and then levels off with only small changes. From Table I and (21), we find that the former effect is due to the substantial increase in  $\hat{l}(0)$  from the first- to the second-row elements. The increase is large enough to smother the effect of the change in  $\hat{l}(1)$ ; this is perhaps surprising inasmuch as the unique properties of the first-row elements are usually attributed<sup>3,4</sup> to a strong  $l=1$  component of the potential arising from the absence of core  $p$  states. The behavior among the heavier elements results from small changes in  $\hat{l}(0)$  and  $\hat{l}(1)$ , which tend to cancel. We conclude that the attractive-repulsive balance in (21) is sufficient to rationalize trends in  $q_0$ .

#### D. Trends in Core and Atomic Radii

It is occasionally preferable to frame discussions of structural trends in solids in terms of the core radius  $r_c$  rather than the form-factor mode  $q_0$ .<sup>4</sup> Certainly a transformation to real space is convenient if comparisons are to be made between solids and molecules. Here we show that as they are defined by the Pauli-force model potential,  $q_0$  and  $r_c$  are equivalent in chemical content.

For the local form of our model potential [Eq. (5)], (18) becomes

$$q_0^{1\text{oc}} = 2Z/\hat{B}_1. \quad (22)$$

Recalling the definition (6) of the local core radius, we obtain

$$q_0^{1\text{oc}} r_c^{1\text{oc}} = 4/\pi. \quad (23)$$

Equation (23) is reminiscent of a result of Ashcroft's "empty-core" model,<sup>13</sup>

$$q_0 r_c = \frac{1}{2}\pi. \quad (24)$$

This similarity between relations derived from quite different model potentials suggests that an inverse proportionality between  $q_0$  and  $r_c$  may exist generally.

Now if the definition (6) is extended to a nonlocal potential so that

$$r_c(l) \equiv 2\hat{B}_l/Z, \quad (25)$$

we can write the summation in (18) as a weighted sum of  $l$ -dependent core radii:

$$2 \sum_l \hat{B}_l P_l \left(1 - \frac{q_0^2}{2k_F^2}\right) / Z = \sum_l r_c(l) P_l \left(1 - \frac{q_0^2}{2k_F^2}\right). \quad (26)$$

This last relation implies a tentative definition of the core radius of an atom in a solid,

$$r_c \equiv N \sum_l r_c(l) P_l \left(1 - \frac{q_0^2}{2k_F^2}\right), \quad (27)$$

where  $N$  is some appropriate normalization factor. The arguments of the Legendre-polynomial weighting factors have been chosen so as to generate a

relation between  $q_0$  and  $r_c$  of the form of (23) and (24). In fact, combining (27) and (18), we find that such a relation holds to the degree that

$$q_0/2k_F \approx \text{const}. \quad (28)$$

We have already remarked, in the discussion following (18), that (28) is a good approximation over much of the Periodic Table. It now becomes clear that this result, which we introduced earlier as an empirical observation, can be regarded as a consequence of the inverse relationship between  $q_0$  and  $r_c$ . Making use of (19) in (26) and (27), we finally obtain

$$r_c \approx C \sum_l \frac{\hat{B}_l}{Z} P_l(-0.345), \quad (29)$$

where  $C$  is a constant.

It is informative to compare (29) with the atomic radius  $r_A$ . Recalling the definition  $k_F \equiv (3\pi^2 Z/\Omega)^{1/3}$ , and applying (28) and (20), we have

$$r_A \approx C \sum_l \frac{\hat{B}_l}{Z^{2/3}} P_l(-0.345), \quad (30)$$

where  $C$  is a constant, not the same as in (29). Both atomic and core radii increase with an increase in the repulsive part of the potential, and decrease with an increase in the core charge  $Z$ , in accord with chemical intuition. Moreover, comparing (29) with (30), we obtain the relation

$$r_c/r_A \propto Z^{-1/3}, \quad (31)$$

which states that as the net core charge increases, the core radius decreases faster than the atomic radius. The same result has been noted by Heine and Weaire,<sup>4</sup> and is closely related to the trend toward more open structures from left to right across the Periodic Table.

#### E. Relation to Local Model Potentials

Simplifying approximations to the pseudopotential form factor have often taken the form of local model potentials characterized by one or more adjustable parameters which can be fitted to experimental data or to the results of more sophisticated calculations. We can make contact with this work by fitting these parameters instead to the results of Secs. IIIA-III D.

For example, the adjustable parameter in Ashcroft's "empty-core" model potential,<sup>13</sup>

$$V^A(r) = 0, \quad r < r_c \\ = -Z/r, \quad r > r_c \quad (32)$$

is, of course, the core radius  $r_c$ . If it is chosen so as to give the accurate value (20) for  $q_0$  in the form factor, then according to (24), Ashcroft's core radius  $r_c^A$  differs from (29) only by a factor  $q_0/2k_F$ :

$$r_c^A = \frac{1}{2}\pi^2 \frac{q_0}{2k_F} \sum_l \frac{\hat{B}_l}{Z} P_l(-0.345). \quad (33)$$

The similarity of (33) to (29), though predictable from (23) and (24), may appear surprising at first glance, since the "empty-core" and Pauli-force model potentials are grounded in rather different physics. However, it is quite in keeping with our discussion of the cancellation theorem that the core radius chosen to give the best cancellation should be a weighted average of  $l$ -dependent core radii like (27). In the approximation (28), we recover (29) from (33), and a discussion of chemical trends in the Ashcroft core radius proceeds along precisely the lines of Sec. IIIA-III D.

To investigate another local model, suppose that we make the gross approximation of replacing the summation in (17a) with the summation on the right-hand side of (18):

$$\sum_l \hat{B}_l P_l \left(1 - \frac{q^2}{2k_F^2}\right) \approx \sum_l \hat{B}_l P_l \left(1 - \frac{q_0^2}{2k_F^2}\right) \quad (34)$$

for all  $q \leq 2k_F$ . The resulting form factor is

$$V^H(q) = \frac{-4\pi Z}{\Omega \epsilon(q)} \left(\frac{1}{q^2} - \frac{1}{q_0^2}\right), \quad (35)$$

which retains the correct behavior at  $q = 0$  and  $q = q_0$ . We have labeled this result with the superscript  $H$ , because  $V^H(q)$  is simply the Fourier transform of Harrison's early "point-ion" local model potential,<sup>25</sup>

$$V^H(r) = -Z/r + \beta \delta(r). \quad (36)$$

The present "derivation" makes it clear that the effective strength  $\beta$  of the Harrison  $\delta$  function is given by a weighted sum of the Pauli-force parameters  $\hat{B}_l$ :

$$\beta = \frac{2\pi^2}{k_F} \sum_l \hat{B}_l P_l \left(1 - \frac{q_0^2}{2k_F^2}\right). \quad (37)$$

It also invests  $\beta$  with a degree of chemical content in that its dependence upon atomic structure is explicitly displayed. Further, it is apparent that the Harrison potential should be a rather good approximation when (34) is valid—that is to say, when  $\hat{B}_0 \gg \hat{B}_l$  for all  $l > 0$ . This is, of course, just the situation among the first-row elements, whose form factors are in fact represented with reasonable accuracy by  $V^H(q)$ .

#### IV. CONCLUDING REMARKS

The thrust of this work has been twofold—to set forth the physical and mathematical foundations of the Pauli-force model potential, and to establish its chemical utility. Toward the second end, we have contented ourselves with deriving simple, physically intelligible expressions for a few crucial structural parameters, and have reserved more detailed calculations and systematic analysis of structural trends for later publication.<sup>21</sup> Clearly, given our expressions for  $q_0$ ,  $r_c$ , and  $r_A$ , much of

this analysis can proceed along the lines laid out by Heine and Weaire,<sup>4</sup> but with the advantage of a more explicit connection with chemical trends in atomic structure. It is worth remarking, however, that because our potential is useful in real space as well as reciprocal space, analysis from a rather different point of view is often profitable. One example is the work of Simons<sup>5</sup> and of Barthelot and Durand<sup>11</sup> on molecules. As another, we have shown elsewhere<sup>26</sup> that the parameters  $\hat{l}(l)$  as determined in the Appendix define a "structural index," general for  $s$ - $p$  bonded elemental solids, which distinguishes quantitatively among hcp, fcc, bcc, and covalent structures. Further inquiry along these lines is in progress.

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#### APPENDIX

We offer here a simple prescription whereby reasonably accurate values of  $\hat{l}(l)$  may be obtained, by inspection, from the  $l'$  values at the lowest valence energy levels of the one-valence-electron ion.<sup>5</sup> We emphasize that these approximations are not necessarily adequate for detailed calculations of  $V(q)$ , but we have found them sufficiently accurate in the vicinity of  $q_0$  to justify their use in the context of Sec. III B.

(1) For all  $s$ - $p$  bonded elements, let  $\hat{l}(0) = l'(0)$ , and let  $\hat{l}(l) = l$  for  $l \geq 3$ . The former approximation is justified because the lowest valence energy level of the ion is close to  $E_F$ , the latter because the higher  $\hat{l}$ 's and  $l'$ 's are close to their respective  $l$  values<sup>5</sup> and make negligible contributions to the pseudopotential.

(2) For first-row elements, let  $\hat{l}(1) = 1$ ; for other elements, let  $\hat{l}(1) = l'(1)$ . The  $l'(1)$ 's of first-row ions are already close to unity<sup>5</sup> and extrapolation brings them even closer, rendering the  $p$  term relatively unimportant. For the remainder of the Periodic Table, we adopt the ionic  $l'(1)$  without modification. Among the second-row elements,  $l'(1, E)$  is a very weak function of the energy, and our error is small. Among the heavier elements,  $l'(1)$  is greater than 1 and decreases with extrapolation, so that we somewhat overestimate  $\hat{l}(1)$ . On the other hand, for this group  $q_0/2k_F > 0.82$ , so that the approximation (19) underestimates the (negative) value of  $\hat{B}_l(1 - q_0^2/2k_F^2)$  in (18). The two errors tend to cancel in (20), and our final results indicate that their combined effect is small.

(3) For elements with low-lying  $d$  valence levels (K, Rb, Cs, Ca, Sr, Ba), let  $\hat{l}(2) = l'(2)$ ; for other elements, let  $\hat{l}(2) = 2$ . For the first set of elements, the  $d$  contribution to the pseudopotential is important; the validity of a simple extrapolation is

questionable, however, and we simply set  $\hat{l}(2) = l'(2)$ . For the remaining elements, linear extrapolations typically increase  $\hat{l}(2)$  when  $l'(2) < 2$  and decrease  $\hat{l}(2)$  when  $l'(2) > 2$ . As examples, for Al,  $l'(2) = 1.95$  and  $\hat{l}(2) = 1.98$ ; for Si,  $l'(2) = 1.94$  and  $\hat{l}(2) = 1.96$ ; for Ga,  $l'(2) = 2.08$  and  $\hat{l}(2) = 2.00$ ; and for Tl,  $l'(2) = 2.24$  and  $\hat{l}(2) = 2.07$ . We con-

clude that the extrapolation increases the hydrogenic character of the core and leaves a smaller  $d$  contribution to the potential. Hence, for elements without low-lying  $d$  states,  $\hat{l}(2) = 2$  is a good approximation. (Values of  $\hat{l}$  determined by these rules for 30 elements are given in Table I.)

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