THEORETICAL DETERMINATION OF THE COHESIVE ENERGY, THE LATTICE PARAMETER AND THE COMPRESSIBILITY OF LiF CRYSTALS*

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Abstract—The cohesive energy, the lattice parameter, and the compressibility of the static LiF crystal have been determined in the Heitler–London scheme by means of three different quantum mechanical approximations. The first approximation corresponds to the free ion model. In the second approximation the radial deformation of F^--ion due to the crystal field was taken into account by scaling the extensive $2p$-wave functions. In the third approximation, also the deformation of Li^+-ion was taken into account by coupling the above $2p$-scaling and the uniform over-all scaling together. The values of the scaling factors were calculated as a function of interionic distance by treating them as variational parameters. The results obtained from different approximations agree well with the corresponding experimental data. However, certain improvements are gained when using the deformation model of the ions. The virial theorem, a necessary condition for an exact wave function, is satisfied in the third approximation too. The values of the scaling parameters indicate that in the crystal F^--ions are contracted and Li^+-ions slightly extended as compared to the free ion states.

INTRODUCTION

IN THE quantum mechanical calculations of the cohesive energies and of the related quantities for certain ionic crystals[1,2] the Heitler–London approximation using the spin atomic orbitals of the free ions has proved very successful. The theoretical values obtained in this way for the cohesive energy and the lattice parameter agree well with the corresponding experimental data. Theoretical values for the elastic constants deviate of course more from the experimental ones, because they are determined by the second derivatives of the cohesive energy.

There is, however, both experimental and theoretical evidence that the free ion model of even the simplest ionic crystals is to some extent oversimplified. For instance, KORHONEN's[3] and KORHONEN's and VIHINEN's[4] analysis of the experimental structure amplitudes of alkali halide crystals indicate that an observable deformation appears in the outer shells of the negative ions. Furthermore, LÖWDIN and FRÖMAN[5] have shown that the virial theorem

$$\Delta T = -E_{\text{coh}} \quad (\Delta T = T_{\text{cr}} - T_f)$$
$$\Delta V = 2E_{\text{coh}} \quad (\Delta V = V_{\text{cr}} - V_f) \quad (1)$$

is not fulfilled at all at the crystal equilibrium in the case of the free ion model. In equation (1) T_{cr}, V_{cr}, T_f and V_f are the kinetic and potential energies of the crystal and of the free ion system, respectively, while E_{coh} represents the cohesive energy of the crystal. In fact, from equation (1) we can conclude that the free ions, due to the crystal field, are deformed in such a way that the

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kinetic and potential energies of the free ion system will change according to the virial theorem. As shown by LÖWDIN and FRÖMAN[5] the virial theorem can be fulfilled by scaling uniformly all the electron and nuclear co-ordinates. Based on the variational principle the above scaling procedure also lowers the value of the cohesive energy. Furthermore, it makes small improvements in the values of lattice parameter and of compressibility. The preliminary reports of this work[6] contains quite a detailed discussion of why the cohesive properties of the crystals cannot change very much in the uniform over-all scaling.

The overlap of the ions in the crystal is mainly due to the overlap occurring between the wave functions of the outer shells of the neighbouring ions. In addition, the outer shell electrons are loosely bound as compared to the inner shell electrons. Therefore, the charge clouds contributed by the outer shell electrons are the more easily deformable. These facts then suggest that the deformation of the ions in the ionic crystals would mainly be due to the deformation of the outer shell wave functions. This picture is supported by the experiments mentioned above.[3,4] In the case of LiF the deformation will mainly take place in the 2p-orbitals if we accept the above deformation picture.

In the present paper the cohesive energy, the lattice parameter, and the compressibility of the LiF crystal have been determined by deforming the radial wave functions in the 2p-shell of F^--ion by means of the scaling method. The virial theorem (1) has also been taken into account by making the uniform over-all scaling after the partial 2p-scaling of the F^--ion. The theoretical results refer, of course, to a static lattice and therefore correspond approximately to a situation at $0°K$. Furthermore, the exchange and overlap energies as well as the correction to the electrostatic energy due to the finite size of the ions have been calculated within the nearest neighbour approximation.

EXPRESSION FOR THE COHESIVE ENERGY OF IONIC CRYSTALS BY USING RADIALLY DEFORMED ATOMIC ORBITALS

Let the set of functions $(\phi_1, \phi_2, ...)$ represent the atomic orbitals for the free ions. This set of functions thus determines the density matrix of the crystal[5]

$$\rho^{(0)}(1,1') = \sum_{\nu,\mu}^{\text{all}} \phi_\nu(1)\Delta^{-1}{}_{\nu\mu}\phi_\mu{}^*(1')[\alpha_1\alpha_1'+\beta_1\beta_1'] \quad (2)$$

in the free ion approximation. We introduce now the new basic set $(\Psi_1, \Psi', ... \Psi_N)$, deformed atomic orbitals, the members of which are related to the ϕ-set as follows:

$$\Psi_\nu = \eta^{3/2}\phi_\nu(\eta r,\theta,\Phi)$$

$$\eta = 1+\sigma \text{ for some values of } \nu$$
$$\eta = 1 \text{ for all the other values of } \nu. \quad (3)$$

Equation (3) simply means that we have formed the new basic set by scaling radially the co-ordinates of some electrons. The factor $\eta^{3/2}$ in equation (3) preserves the normalization of the wave functions. Now the experimental data point out that the deformation of the ions is small in the alkali halides.[3,4] This means that the parameter σ in (3) is not in practice very far from zero. Thus it is reasonable to expand (3) into Taylor's series around the point r, and we get

$$\Psi_\nu = \phi_\nu(r,\theta,\Phi)+\psi_\nu(r,\theta,\Phi)\sigma+\varphi_\nu(r,\theta,\Phi)\sigma^2+[\sigma^3] \quad (4)$$

For the wave functions separable in the radial and angular parts, the expansion (4) is

$$\Psi_\nu = k_{lm}\left[\frac{f_{nl}(r)}{r} + \frac{f_{1nl}(r)}{r}\sigma + \frac{f_{2nl}(r)}{r}\sigma^2 + [\sigma^3]\right]Y_{lm}(\theta,\Phi). \quad (5)$$

In equation (5) k_{lm} is the normalization constant, $Y_{lm}(\theta,\Phi)$ represents the spherical harmonic, and the radial functions f_{1nl} and f_{2nl} have the expressions

$$f_{1nl} = \tfrac{1}{2}f_{nl}(r)+f_{nl}'(r)r,$$
$$f_{2nl} = -\tfrac{1}{8}f_{nl}(r)+\tfrac{1}{2}f_{nl}'(r)r+\tfrac{1}{2}f_{nl}''(r)r^2 \quad (6)$$

In (6) the primes denote the derivatives of $f_{nl}(r)$ with respect to r. By comparing (4) and (5) we find that

$$\phi_\nu = k_{lm}\frac{f_{nl}}{r}Y_{lm},$$

$$\psi_\nu = k_{lm}\frac{f_{1nl}}{r}Y_{lm},$$

$$\varphi_\nu = k_{lm}\frac{f_{2nl}}{r}Y_{lm}. \quad (7)$$

For practical computations the radial functions f_{1nl} and f_{2nl} can be tabulated according to equation (6), if the free ion wave functions are available only in a numerical form.

The density matrix of the crystal can now be expressed with the power series expansion

$$\rho(1,1',\sigma) = \rho^{(0)}(1,1') + \rho^{(1)}(1,1)\sigma + \rho^{(2)}(1,1')\sigma^2 + [\sigma^3],$$

(8)

where

$$\rho^{(0)}(1,1') = \sum_{\nu,\mu}^{all} \phi_\nu \Delta^{-1}{}_{\nu\mu} \phi_\mu^* [\alpha_1\alpha_1' + \beta_1\beta_1']$$

$$\rho^{(1)}(1,1') = \sum_{\nu,\mu}^{all} [\phi_\nu \Delta^{-1}{}_{\nu\mu}\psi_\mu^* + \psi_\nu \Delta^{-1}{}_{\nu\mu}\phi_\mu^*$$
$$- \phi_\nu \mathfrak{R}^{(1)}{}_{\nu\mu}\phi_\mu^*][\alpha_1\alpha_1' + \beta_1\beta_1'] \quad (9)$$

$$\rho^{(2)}(1,1') = \sum_{\nu,\mu}^{all} [\phi_\nu \Delta^{-1}{}_{\nu\mu}\varphi_\mu^* + \varphi_\nu \Delta^{-1}{}_{\nu\mu}\phi_\mu^*$$
$$+ \psi_\nu \Delta^{-1}{}_{\nu\mu}\psi_\mu^* - \phi_\nu \mathfrak{R}^{(1)}{}_{\nu\mu}\psi_\nu^* - \psi_\mu \mathfrak{R}^{(1)}{}_{\nu\mu}\phi_\mu$$
$$- \phi_\nu \mathfrak{R}^{(2)}{}_{\nu\mu}\phi_\mu^*][\alpha_1\alpha_1' + \beta_1\beta_1'].$$

In (9) $\Delta^{-1}{}_{\nu\mu}$ is an element of the inverse overlap matrix for the free ion wave functions, while $\mathfrak{R}^{(1)}{}_{\nu\mu}$ and $\mathfrak{R}^{(2)}{}_{\nu\mu}$ are the elements of the matrices defined as

$$\mathfrak{R}^{(1)} = \Delta^{-1}\Delta^{(1)}\Delta^{-1},$$
$$\mathfrak{R}^{(2)} = \Delta^{-1}\Delta^{(2)}\Delta^{-1} - \Delta^{-1}\Delta^{(1)}\Delta^{-1}\Delta^{(1)}\Delta^{-1}. \quad (10)$$

In (10) the matrices $\Delta^{(1)}$ and $\Delta^{(2)}$ are defined by relations

$$\Delta^{(1)}{}_{\nu\mu} = \int (\phi_\nu^*\psi_\mu + \psi_\nu^*\phi_\mu)\, d\tau$$

$$\Delta^{(2)}{}_{\nu\mu} = \int (\phi_\nu^*\varphi_\mu + \psi_\nu^*\psi_\mu + \varphi_\nu^*\phi_\mu)\, d\tau. \quad (11)$$

In the first approximation we obtain

$$\mathfrak{R}^{(1)} \simeq \Delta^{(1)} \quad \text{and} \quad \mathfrak{R}^{(2)} \simeq \Delta^{(2)}. \quad (12)$$

We see in equation (8) that the first member in the expansion is just the density matrix of the crystal composed of free ions. By utilizing the normalization property of the wave functions, we obtain for the trace of the density matrix an equation

$$Tr\rho^{(1)}(1,1')\sigma + Tr\rho^{(2)}(1,1')\sigma^2 + Tr[\sigma^3] = 0, \quad (13)$$

which means that the coefficients of σ in the expansion (13) must vanish identically. Physically this means that the net electronic charge associated with the density matrices $\rho^{(1)}$, $\rho^{(2)}$, ... equals zero. This is a very important property because in this case the energy contributions resulting from $\rho^{(1)}$, $\rho^{(2)}$ ... are rapidly convergent with increasing internuclear distances in the crystal.

For the cohesive energy we obtain by means of the expansion (8) the following:

$$E_{coh} = E^{(0)} + E^{(1)}\sigma + E^{(2)}\sigma^2 + [\sigma^3]. \quad (14)$$

Here $E^{(0)}$ is just the cohesive energy of the crystal in the free ion approximation. The energy contributions $E^{(1)}$ and $E^{(2)}$ are due to the scaling of the wave functions and their detailed expressions are given in the preliminary report of this work.[6]

In the following treatment we assume that the terms including the third and higher powers of the parameter in the expansion (14) can be neglected as small compared to the three first terms. Within this approximation, the optimum value of σ with respect to the cohesive energy is

$$\sigma_{min} = -\frac{E^{(1)}}{2E^{(2)}}. \quad (15)$$

Consequently the cohesive energy becomes

$$E_{coh} = E^{(0)} - \frac{E^{(1)2}}{4E^{(2)}}. \quad (16)$$

For the rapid convergence of the series expansions, the parameter must be small, or in other words $E^{(1)} \ll E^{(2)}$. In addition, the energy term $E^{(2)}$ should be positive in order to obtain the minimum of the cohesive energy. If the above conditions are satisfied, the simplified energy expression (16) is consistent with the variational principle. Our numerical data for the LiF crystal show the above assumption well justified (cf. Tables 2 and 3). The approximate relations (15) and (16) are obviously valid for all alkali halide crystals because the deformation of the ions are of the same magnitude in these crystals.

In the nearest neighbour approximation, the energy terms $E^{(1)}$ and $E^{(2)}$ (computed per one mole)

can be expressed as

$$E^{(1)} = \sum E_{\mathrm{ion}}{}^{(1)} + 6N_A E_{gg'}{}^{(1)} + 6N_A B_{gg'}{}^{(1)}$$

$$+ 6N_A E_{eff}{}^{(1)},$$

$$E^{(2)} = \sum E_{\mathrm{ion}}{}^{(2)} + 6N_A E_{gg'}{}^{(2)} + 6N_A B_{gg'}{}^{(2)}$$

$$+ 6N_A E_{eff}{}^{(2)}, \qquad (17)$$

which are valid only for an unstrained crystal of the NaCl-type. In equations (17) different energy contributions are due to the scaling of some radial wave functions of the ions. The first term in each equation represents the total internal deformation energy of the ions, the second term is caused by the electrostatic and exchange interactions between the nearest neighbours, the third one is what we refer to as the overlap energy while the last one is due to the fact that the deformed atomic wave functions no longer obey the Hartree–Fock equations for the free ions. The detailed expressions for different energy terms in (17) are given elsewhere.[6]

To be sure that the virial theorem is satisfied in the general form[5]

$$2T + V + a\frac{dE}{da} = 0 \qquad (18)$$

we must couple the uniform over-all scaling and the above partial scaling together in determination of the cohesive energy. If $\eta_0 = 1 + \sigma_0$ is the scale factor for the uniform over-all scaling of the electronic and nuclear co-ordinates, and $\rho = \eta_0 a$ we obtain for the cohesive energy[5]

$$E_{\mathrm{coh}}(\eta_0, a) = \eta_0{}^2 T(1,\rho) + \eta_0 V(1,\rho) - T_f - V_f. \qquad (19)$$

Here $T(1,\rho)$ and $V(1,\rho)$ are the total kinetic and potential energies of the crystal for $\eta_0 = 1$, and T_f and V_f represent the corresponding quantities for the system of free ions. By treating the two scaling factors, η and η_0, as the variational parameters we shall obtain their optimum values from the simultaneous equations

$$A\sigma + C\sigma_0 + D = 0$$

$$C\sigma + B\sigma_0 + E = 0 \qquad (20)$$

The coefficients of σ and σ_0 in (20) have the

expressions[6]

$$A = E^{(2)}, \quad B = \Delta T^{(0)} + T_f, \quad C = (T^{(1)} + E^{(1)})/2,$$

$$D = E^{(1)}/2, \quad \text{and} \quad E = (\Delta T^{(0)} + E_{\mathrm{coh}}{}^{(0)})/2. \qquad (21)$$

NUMERICAL RESULTS FOR LiF CRYSTAL

The cohesive energy, the lattice parameter, and the compressibility of LiF crystal were determined as an application of formulae (2)–(21) in the present work. SCF-wave functions with exchange calculated by SACHS[7] were used for the determination of these quantities. The above wave functions have been reported to have a self-consistency of up to 5 decimals. Simpson's integration rule in a slightly modified form was used for the numerical integrations. The two-centre integrals in the expression of the cohesive energy were computed by expanding the wave functions centred at a certain nucleus into the spherical harmonics around another nucleus as represented by LÖWDIN.[1] Both the free ion and the deformed ion approximations were used for the present computations. In this way, the results of different approximate models are more easily comparable and the conclusions made from the results are more reliable.

In Table 1 we have compiled the energy contributions appearing in the cohesive energy of the free ion model. Here a is the nearest neighbour distance, E_M = the Madelung energy, E_{corr} the Coulomb correction to the Madelung energy, $C_{gg'}$ the exchange energy, and $B_{gg'}$ the overlap energy. The cohesive energy $E^{(0)}$ is the sum of the above energy terms. The sum $E_{\mathrm{corr}} + C_{gg'} + B_{gg'} = E_{\mathrm{rep}}$ formally corresponds to the repulsion energy of the classical Born–Mayer model of ionic crystals. The equilibrium distance $a_0 = 3\cdot896\, L_H = 2\cdot061$ Å is obtained from the values of the cohesive energy in Table 1. The corresponding value of the cohesive energy is $-6368\cdot1\, E_H$/ion pair $= -239\cdot6$ kcal/mole. The compressibility then takes the value $1\cdot73 \times 10^{-12}$ cm²/dyne.

As mentioned before the most considerable overlap in LiF occurs between the $2p$- and $1s$-wave functions of F^- and Li^+-ion, respectively. Furthermore, the $2p$-wave functions of F^- are more easily deformable than the other wave functions because of their diffuse behaviour. Therefore we have thought it physically reasonable to determine the cohesive energy by scaling separately the $2p$-

Table 1. *Various energy contributions to the cohesive energy of* LiF *in the free ion approximation. Energies are expressed per ion pair in units* $10^{-5} \times E_H (E_H = 1$ *Hartree unit)*

$(L^a{}_H)$	E_M	$E_{corr.}$	$C_{gg'}$	$B_{gg'}$	E_{rep}	$E^{(0)}$
3·70	−7871·9	218·1	−812·8	2146·8	1552·1	−6319·8
3·80	−7664·7				1306·8*	−6357·9
3·90	−7468·2	160·4	−550·0	1489·8	1100·2	−6368·0
4·00	−7281·5				926·4*	−6355·1
4·10	−7103·9	118·8	−377·8	1039·0	780·0	−6323·9

* Interpolated logarithmically.

Table 2. *Various energy contributions to the first order energy term* $E^{(1)}$ *per ion pair in units* $10^{-5} \times E_H$

$(L^a{}_H)$	$E_{gg'}{}^{(1)}$	$B_{gg'}{}^{(1)}$	$E_{eff}{}^{(1)}$	$E^{(1)}$
3·70	1235	−7400	−751	−6916
3·80				−5942*
3·90	935	−5553	−486	−5104
4·00				−4377*
4·10	678	−4149	−283	−3754

* Interpolated logarithmically.

orbitals of F⁻-ion. According to equation (16) we then have

$$E_{coh} = E^{(0)} - E_D,$$

where $E_D = E^{(1)^2}/4E^{(2)}$. Tables 2 and 3 contain energy contributions to the first and second order

Table 3. *Various energy contributions to the second order energy term* $E^{(2)}$ *per ion pair in units* $10^{-5} \times E_H$

$(L^a{}_H)$	$E_{ion}{}^{(2)}$	$E_{gg'}{}^{(2)}$	$E^{(2)}$
3·70	128,485	4,754	133,239
3·80	128,485	4,116	132,601
3·90	128,485	3,566	132,051
4·00	128,485	3,091	131,576
4·10	128,485	2,686	131,171

terms $E^{(1)}$ and $E^{(2)}$, respectively. The ionic term $E_{ion}{}^{(1)}$ is identically equal to zero because the wave functions used for the computations are SCF-wave functions. Furthermore, we observe that the ionic term $E_{ion}{}^{(2)}$ is positive and large as compared to the contribution $E_{gg'}{}^{(2)}$ which in turn

is of the same order of magnitude as $B_{gg'}{}^{(2)}$ and $E_{eff}{}^{(2)}$. Therefore, we have neglected the last two terms in $E^{(2)}$.

Table 4. *The optimum values of* σ *and the deformation energy as a function of the internuclear distance*

$(L^a{}_H)$	σ	E_D $(10^{-5} \times E_H)$
3·70	0·0260	89·7
3·80	0·0224	66·6
3·90	0·0193	49·3
4·00	0·0166	36·4
4·10	0·0143	26·9

In Table 4 we have represented the optimum values of the scaling parameter σ and the deformation energy E_D as a function of the internuclear distance. We find from Table 4 that the scaling parameter is positive in sign which physically means that the F⁻-ions are slightly contracted in the crystalline state. This contraction, of course, increases the kinetic energy of the electrons in

F⁻-ion. The increase of the kinetic energy is about 400 kcal/mole in LiF and it varies with the internuclear distance. This means that we must also work out the uniform over-all scaling by means of formulae (18)–(21) in order to get the virial theorem fulfilled. Table 5 shows the values of the cohesive energy of LiF in the $2p$-scaling.

Table 5. *The cohesive energy of LiF crystal in the* $2p$-*scaling of F⁻-ion as a function of the internuclear distance in units* $10^{-5} \times E_H$

(L^a_H)	$E^{(0)}$	E_D	E_{coh}
3·70	−6319·8	89·7	−6409·5
3·80	−6357·9	66·6	−6424·5
3·90	−6368·0	49·3	−6417·3
4·00	−6355·1	36·4	−6391·5
4·10	−6323·9	26·9	−6350·8

From the data in this Table we can determine the following values for the equilibrium distance, the cohesive energy, and the compressibility: $a_0 = 3·817$, $L_H = 2·019$ Å, $E_{coh} = -241·7$ kcal/mole, $\beta = 1·7 \times 10^{-12}$ cm²/dyne. In Table 6

Table 6. *The cohesive energy and the scaling parameters* σ *and* σ_0 *as a function of the internuclear distance obtained by the simultaneous* $2p$- *and over-all scaling in LiF*

(L^ρ_H)	σ	σ_0	E_{coh}
3·70	0·03350	−0·00354	−6424·4
3·80	0·02819	−0·00271	−6433·7
3·90	0·02357	−0·00197	−6421·9
4·00	0·01951	−0·00133	−6393·6
4·10	0·01601	−0·00078	−6351·5

we have given the cohesive energy and the scaling parameters σ and σ_0 as a function of the internuclear distance. In Table 7 we have collected theoretical results obtained by different investigators for LiF crystal.

The results in Table 7 show that the deformed ion model of the present work gives remarkable improvements in the values of the cohesive energy and of the lattice parameter as compared to the

corresponding free ion approximation. The value of the compressibility is not, however, changed when going from one approximation to another. Furthermore, we observe that the theoretical values of the compressibility of different investigators are systematically too large, with the exception of the value reported by LÖWDIN.[2] Löwdin's value for the compressibility is, however, based on the wave functions, which were not as accurate as those in the present work. The above values of the compressibility simply show that the theoretical crystal composed by the Hartree–Fock ions are too easily compressible. This is only natural because the HF-wave functions are more extensive than the exact wave functions of the free ions. Consequently, it is easier to compress the Hartree–Fock crystal than the real crystal. Thus, in order to improve further the theoretical values of the compressibility we should know, for the computations, more accurate wave functions both for the free ions and for the ions in a crystalline state. For the conclusions drawn above to hold, however, the Heitler–London approximation for the ionic crystals must be justified to a high degree of accuracy. Furthermore, in the more refined quantum mechanical calculations of the above quantities one should also consider the energy contributions due to the van der Waals interactions and to the next nearest interactions between negative ions. These higher order energy terms are of great importance for instance when inspecting the stability of different crystal structures at high pressure. For LiF crystal, the van der Waals energy, including the dipole–dipole and the dipole–quadrupole interaction terms is estimated to be −4·5 kcal/mole[12] at 0°K, while the zero point energy has the value of 3·0 kcal/mole.[13] According to YAMASHITA's[11] quantum mechanical computations, the contributions resulting from the next nearest F⁻-ion interactions were quite small as compared to the terms due to the nearest neighbour interactions for LiF crystal. This result may be accidental and cannot, of course, be generalized to the other alkali halide crystals. Consequently, the sum of these energy contributions is about −1·5 kcal/mole, and hence, the theoretical value of the cohesive energy would be −243–244 kcal/mole. However, in order to take these energy contributions more quantitatively into account a more accurate quantum mechanical treatment of

Table 7. *The cohesive energy and related quantities obtained for LiF by different investigators*

$2a_0$ (Å)	β (10^{-12} cm²/dyne)	E_{coh} (kcal/mole)	Reference	Method
4·01	1·4	−244	8, 9, 10	Exp.
4·00	1·96	−239	11	Theor.[1]
4·20	1·3	−222	2	Theor.[2]
4·12	1·7	−240	Present work	Theor.[3]
4·04	1·7	−241	Present work	Theor.[4]
4·03	1·7	−242	Present work	Theor.[5]

[1] Analytical variation of the $2p$-wave functions.
[2] Free ion SCF-wave functions with exchange having selfconsistency up to 3 decimals.
[3] Free ion SCF-wave functions with exchange having selfconsistency up to 5 decimals.
[4] $2p$-scaling of free ion SCF-wave functions with exchange.
[5] Coupled $2p$-scaling and uniform over-all scaling of free ion SCF-wave functions with exchange.

the van der Waals interactions would be necessary for ionic crystals.

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