

Ab-initio effective potentials in crystal Hartree-Fock theory

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Abstract. *Ab initio* effective potential technique of Ewig *et al* is applicable directly to crystal Hartree-Fock formalism provided the effective potentials are suitably defined. Corresponding to every atom or every molecule by constructing a crystal one can assign a unit species configuration. The effective potentials in the crystal can be expressed as functions of lattice parameters in terms of integrals over the orbitals of this unit species. These expressions are in a more exact form than those usually employed in molecular calculations.

Keywords. Crystal Hartree-Fock; effective potentials; species configuration.

1. Introduction

The last decade has seen the development of *ab initio* Hartree-Fock Self-Consistent-Field (HFSCF) treatment for crystalline systems (Collins *et al* 1974; Dagens and Perrot 1972; Euwema *et al* 1973, 1974; Harris and Monkhorst 1969; Kunz 1969, 1971, 1972; Kunz *et al* 1973; Mickish *et al* 1974; Surratt *et al* 1973). Various symmetry operations render such a calculation feasible in practice for crystals containing atoms of mostly upto the second row in the periodic table. For a crystal of heavier atoms the standard difficulties of an *ab-initio* HFSCF calculations of a large system are met. This leads one to look for *ab initio* effective potential techniques which translate the HFSCF theory in terms of a valence electronic Hamiltonian and mutually orthonormal valence pseudofunctions which are otherwise unconstrained in nature (Ewig *et al* 1975, 1977; Kahn and Goddard 1972; Kahn *et al* 1976; Datta *et al* 1978). The primary objective of such techniques is to make accurate calculations on a large system possible. The critical step in such a procedure is to choose a facile means of producing effective potentials in an *ab initio* fashion. This work stems from the hope that once the effective potentials are reasonably expressed for crystals, the HFSCF procedure using the effective potential technique will be a routine for crystals of heavier atoms (such as Si or Ge semiconductors).

In this work we discuss the generation of crystal effective potentials in the Ewig sense. Thus these potentials consist of two parts, one coming from the one-electronic modification of the Fock operator (Phillips-Kleinman pseudopotential) and the second one representing modifications of the two-electronic repulsions (Ewig W potentials). The core-valence interactions are grouped into W^{core} potentials whereas the change in valence-valence interactions is given by W^{val} potentials. In molecular calculations the SCF iterations give results which are very sensitive to

W^{val} potential and one expects such a trend to be more prominent for calculations on crystals. This work describes the choice of crystal Phillips-Kleinman pseudo-potential and W -potentials with as little approximation as possible in them.

2. Effective potential treatment for crystals

We consider a crystal of N unit cells where the position of the centre of a th unit species or the i th electron is given by the position vectors \mathbf{R}_a or \mathbf{r}_i . The a th type of local basis function in the a th unit species is denoted by $\psi_a(\mathbf{r}-\mathbf{R}_a)$ and the corresponding Bloch orbital $\phi_a^k(\mathbf{r})$ is written as normalised Fourier transform of the ψ 's. The crystal orbital $\Psi_n^k(\mathbf{r})$ is expressed as a linear combination of the Bloch orbitals ϕ_a^k where n is a band index. The HFSCF theory leads to the pseudo-eigenvalue condition

$$\mathcal{F} \Psi_n^k(\mathbf{r}_1) = \epsilon_n^k \Psi_n^k(\mathbf{r}_1) \quad (1)$$

where

$$\mathcal{F} = -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_1}^2 - e^2 \sum_{an}^{\text{nuclei}} \frac{Zan}{|\mathbf{r}_1 - \mathbf{R}_{an}|} + e^2 \int d\mathbf{r}_2 |\mathbf{r}_1 - \mathbf{r}_2|^{-1} [2 - P_{12}]_{\mathbf{r}_2 = \mathbf{r}'_2} \rho(\mathbf{r}_2, \mathbf{r}'_2).$$

Thus the crystal Fock operator \mathcal{F} is expressed in terms of the single-particle density $\rho(\mathbf{r}, \mathbf{r}')$ evaluated over the crystal orbitals. Full crystal symmetry is retained in ρ .

Provided the orbitals of the system are divided into strongly orthogonal core and valence sets and if frozen-core assumption holds good, minimisation of the total energy is equivalent to the minimisation of $E_v + \tilde{V}_{nn}$, where E_v is the valence electronic energy containing all core-valence and valence-valence interactions and \tilde{V}_{nn} is the screened nuclear-nuclear repulsion. The core orbitals are then N -fold degenerate and the corresponding single-particle density ρ^{core} has the full crystal symmetry. The valence single particle density ρ^{val} should also have this symmetry. The minimisation condition translates equation (1) into the form:

$$\mathcal{F}_v \Psi_{nv}^k(\mathbf{r}) = \epsilon_{nv}^k \Psi_{nv}^k(\mathbf{r}),$$

where

$$\mathcal{F}_v = h_1 + \sum_a^{\text{units}} \sum_a^{\text{local core}} (2J_{aa}^c - K_{aa}^c) + \sum_{n'k'}^{\text{val}} (2J_{n'k'}^v - K_{n'k'}^v), \quad (2)$$

h_1 being the unchanged one-electronic operator in \mathcal{F} , J and K are the direct and exchange coulomb repulsion operators expressed in terms of the exact orbitals. The valence orbital must be orthogonal to all the core orbitals and all the two-particle interactions involving the valence functions are still retained in \mathcal{F}_v .

Considering a set of arbitrary local valence functions χ 's (pseudofunctions) having the same symmetries as those of the exact local valence functions ψ 's, the Bloch pseudoorbitals and the crystal pseudo-orbitals can be constructed as

$$\Phi_a^k = N^{-1/2} \sum_a \exp(i\mathbf{k} \cdot \mathbf{R}_a) \chi_a(r - R_a), \quad \alpha = \text{valence} \quad (3)$$

$$\text{and} \quad X_{n\gamma}^k = \sum_a' C_{n\alpha}^k \Phi_a^k,$$

where the prime indicates that the summation is to be carried out over only the local valence subset. If \hat{P} is a core projection operator corresponding to all core orbitals

$$\hat{P} = \sum_a^{\text{core}} \hat{P}_a = \sum_a^{\text{units}} \sum_a^{\text{core}} |\psi_{a\alpha}\rangle \langle \psi_{a\alpha}|$$

and χ_γ^{val} is chosen such that $\psi_\gamma^{\text{val}} = (1 - \hat{P}) \chi_\gamma^{\text{val}}$, it necessarily follows that

$$\phi_\gamma^k = (1 - \hat{P}) \Phi_\gamma^k,$$

$$\text{and} \quad \Psi_{n\nu}^k = (1 - \hat{P}) X_{n\nu}^k.$$

this means that the functions χ , Φ and X are approximately equal to ψ , ϕ and Ψ in the valence region of space. The variational condition in (2) is now given by

$$(\mathcal{F}_v + V^{PP}) X_{n\nu}^k = \epsilon_n^k X_{n\nu}^k, \quad (4)$$

where assuming $[\mathcal{F}_v, \psi_a^{\text{core}}] = 0$ the pseudopotential V^{PP} can be written in the Phillips-Kleinman form (Phillips and Kleinman 1959)

$$V^{PP} = - \sum_a \sum_a^{\text{core}} |\psi_{a\alpha}\rangle (\epsilon_a - \epsilon_n^k) \langle \psi_{a\alpha}|. \quad (5)$$

For practical purposes one intends to work with the Fock operator \mathcal{F}_v which is defined in terms of the crystal pseudo-orbitals

$$\hat{\mathcal{F}}_v = h_1 + \sum_{n'k'}' (2 \hat{J}_{n'k'}^v - \hat{K}_{n'k'}^v), \quad (6)$$

$$= h_1 + e^2 \int d\mathbf{r}_2 |\mathbf{r}_1 - \mathbf{r}_2|^{-1} [2 - P_{12}]_{r_2' = r_2} \rho^{\text{val}}(\mathbf{r}_2, r_2')$$

where \hat{J} , \hat{K} and $\hat{\rho}$ are the corresponding operators involving the pseudo-orbitals. Equation (4) is then rewritten as

$$(\hat{\mathcal{F}}_v + V^{PP} + W) X_{nv}^k = \epsilon_n^k X_{nv}^k. \quad (7)$$

W can be obtained from the operator equivalence in (4) and (7) (Ewig *et al* 1975, 1977):

$$W = (\mathcal{F}_v - \hat{\mathcal{F}}_v) X_{nv}^k(\mathbf{r}) / X_{nv}^k(\mathbf{r}) = W_c + W_v, \quad (8)$$

with
$$W_c = \sum_a \sum_a^{\text{core}} (2J_{aa}^c - K_{aa}^c) X_{nv}^k(\mathbf{r}) / X_{nv}^k(\mathbf{r}),$$

and
$$W_v = \sum'_{n'k'} [(2J_{n'k'}^v - K_{n'k'}^v) - (2J_{n'k'}^x - K_{n'k'}^v)] [X_{nv}^k(\mathbf{r}) / X_{uv}^k(\mathbf{r})].$$

Using the expressions of crystal pseudo-orbitals in (3) one obtains the Hartree-Fock-Roothan equation

$$\begin{aligned} \sum'_\gamma \left[\mathcal{F}_{\beta\gamma}^k + \left\{ \epsilon_n^k \sum_a^{\text{core}} (\hat{P}_a)_{\beta\gamma}^k - \sum_a^{\text{core}} \epsilon_a (\hat{P}_a)_{\beta\gamma}^k \right\} \right. \\ \left. + \left\{ (W_c)_{\beta\gamma}^k + (W_v)_{\beta\gamma}^k \right\} \right] C_{n\gamma}^k = \epsilon_n^k \sum'_\gamma 1_{\beta\gamma}^k C_{n\gamma}^k, \end{aligned} \quad (9)$$

where 1 is the unit operator (unity). The \hat{P}_a containing term arises from the Phillips-Kleinman pseudopotential. The matrix elements $\Omega_{\beta\gamma}^k$ are defined as

$$\Omega_{\beta\gamma}^k = N^{-1} \sum_{b,c} \exp [i\mathbf{k}(\mathbf{R}_c - \mathbf{R}_b)] \Omega_{\beta\gamma}(R_b, R_c) \quad (10)$$

where $\Omega_{\beta\gamma}(R_b, R_c) = \langle \chi_{b\beta} | \Omega | \chi_{c\gamma} \rangle$,

$\chi_{b\beta}$ being the short hand notation for $\chi_{b\beta}(\mathbf{r} - \mathbf{R}_b)$. In equation (7), $(V^{PP} + W)$ is the effective potential.

Thus *ab initio* investigation of the electronic properties of a crystal of heavier atoms can be started by solving the matrix eigenvalue equation (9). One may note that the full crystal symmetry is retained in each of the operators $\hat{\mathcal{F}}_v$, \hat{P}_a , W_c and W_v . Since evaluation of the matrix elements of $\hat{\mathcal{F}}_v$ or $\hat{1}$ is direct, in the next section we discuss the simplification of the forms of $\Omega_{\beta\gamma}$ matrix elements for the operators \hat{P}_a , W_c and W_v .

3. Discussion

We consider the following three physical points:

(a) First we show that the different components of the crystal effective potential can be reduced to the unit species form by using periodicity in a crystal. The operators \hat{P}_a and W_c are defined as sums over all unit species (a)

$$(\hat{P}_a)_{\beta\gamma} = \sum_a \langle \chi_{b\beta} | \psi_{a\alpha} \rangle \langle \psi_{a\alpha} | \chi_{c\gamma} \rangle$$

$$\text{and } (W_c)_{\beta\gamma} = \sum_a \langle \chi_{b\beta} | \sum_a^{\text{core}} (2J_{aa}^c - K_{aa}^c) | \chi_{c\gamma} \rangle.$$

Each term in these sums depends only on the relative orientations of \mathbf{R}_a , \mathbf{R}_b and \mathbf{R}_c . The sum over \mathbf{R}_a may be replaced by that over $\mathbf{R}_a - \mathbf{R}_b$ for a large crystal (assuming infinite) such that $\mathbf{R}_b - \mathbf{R}_c$ is held constant. Without loss of generality one can set $\mathbf{R}_a = 0$. Thus the matrix elements of W_c and \hat{P}_a are given by

$$(W_c)_{\beta\gamma} = \int dr_1 dr_2 \sum_a^{\text{core}} \psi_a^*(\mathbf{r}_1) \left\{ \sum_{\substack{n_1 n_2 n_3 \\ -\infty}}^{+\infty} \chi_\beta^*(\mathbf{r}_2 + n) r_{12}^{-1} (2 - P_{12}) \right. \\ \left. \chi_\gamma(\mathbf{r}'_2 + n + \Delta n) \right\} \psi_a(\mathbf{r}'_1), \quad (11a)$$

$$(\hat{P}_a)_{\beta\gamma} = \sum_{\substack{n_1 n_2 n_3 \\ -\infty}}^{+\infty} \int dr \chi_\beta^*(r+n) \psi_a(r) \int dr' \psi_a^*(r') \chi_\gamma(r'+n+\Delta n), \quad (11b)$$

where $\mathbf{R}_b - \mathbf{R}_c$ is denoted by the lattice vector Δn . Equation (11) expresses the Phillips-Kleinman pseudopotential and the core potential as a function of lattice constants using the orbitals of only *one* unit species.

(b) In standard effective potential calculations it is a general practice to assume the atomic W potentials to be transferable to the molecular case. This amounts to saying that the molecular valence Fock operator mimicks the atomic valence Fock operator in the core region of space. If a similar assumption is made in the case of a crystal, some of the repulsions, such as those between an electron on a valence pseudo-orbital of one atom and another electron on a core orbital of another atom, are lost. The presence of a large number of atomic cores in the system would have an appreciable effect on the valence electronic behaviour, and hence one should not take recourse to any such assumption in calculating $(W_c)_{\beta\gamma}$ but can directly use (11a).

(c) However, one may use the assumption of atomic transferability in order to reduce W_v functions for crystals in a convenient unit species form. The transferability is justified if (i) the valence pseudo-orbitals form (approximately) a complete set, (ii) atomic pseudovalence functions are all (approximately) orthogonal and (iii) atomic pseudovalence functions are (approximately) numerically equal to the atomic

valence functions in the valence region of space of another atom. For the crystalline case one may neglect assumption (iii). Considering the first two assumptions which are reminiscent of the idea of a frozen core, the single particle density $\hat{\rho}^{\text{val}}(\mathbf{r}, \mathbf{r}')$ reduces to

$$\begin{aligned}\hat{\rho}^{\text{val}}(\mathbf{r}, \mathbf{r}') &\equiv \sum_{n,k} X_{nv}^{k*}(\mathbf{r}') X_{nv}^k(\mathbf{r}) \\ &= \sum_a \sum_{\beta}' X_{\beta}^*(\mathbf{r}' - \mathbf{R}_a) X_{\beta}(\mathbf{r} - \mathbf{R}_a).\end{aligned}$$

Assuming an infinite crystal $(W_v)_{\beta\gamma}$ is now given by

$$\begin{aligned}(W_v)_{\beta\gamma} &= \int dr_1 dr_2 \left\{ \sum_{\substack{n_1 n_2 n_3 \\ -\infty}}^{+\infty} X_{\beta}^*(r_2 + n) r_{12}^{-1} (2 - P_{1'2'}) X_{\gamma}(r_2' + n + \Delta n) \right\} \\ &\quad \times \sum_{\alpha}' \{ \psi_{\alpha}^*(r_1) \psi_{\alpha}(r_1') - X_{\alpha}^*(r_1) X_{\alpha}(r_1') \}.\end{aligned}\quad (11c)$$

which is in the unit species form.

Table 1. GTO basis for sulphur atom.

Exponents	Coefficients		
	1s	2s	3s
1259-97006	-0-0566	0-003767	
230-55899	-0-259457	0-017198	
64-051814	-0-531444	0-182466	
21-258221	-0-290858	0-14992	
328-0479	-0-000107	0-012546	
56-492561	-0-00049	0-057286	
4-539419	0-005196	-0-607773	
1-730085	0-004269	-0-499368	
6-815986	-0-000057	-0-00003	-0-032955
1-919896	-0-000296	-0-001545	-0-17245
0-344267	0-001289	0-006735	0-75185
0-016938	0-000616	0-003216	0-35896
		2p _z	3p _z
64-48947		0-056474	
16-72116		0-282455	
5-894725		0-545433	
2-34679		0-260201	
6-187882		-0-00078	-0-014343
0-63945		0-014981	0-27552
0-28901		0-031792	0-58468
0-13971		0-011663	0-2144987

Table 2. Different components of crystal potential

$z =$ 0.3883 a.u. x in a.u.	V_{e-n}	W_{val}	W_{total}	V_{PK}^s	V_{PK}^x
0.0	-102.97	0.2436	87.76	4.1165	
0.9709	-76.75	0.0318	71.04	0.9554	0.0158
1.9417	-68.73	0.0149	65.71	0.0261	0.0021
2.9126	-65.06	0.0097	63.02	0.0168	0.0021
3.8835	-62.63	0.0054	61.10	0.0127	0.0020
0.0				324.46	
0.3883	-102.97	0.2436	87.76	4.1165	
0.7767	-82.68	0.0704	75.02	1.3416	
1.1651	-76.37	0.0345	71.25	0.3017	
1.5534	-73.81	0.0286	69.96	0.0216	
1.9417	-73.09	0.0181	70.02	0.0042	
2.3301	-73.81	0.0286	69.96	0.2338	
2.7184	-76.37	0.0345	71.25	2.3885	
3.1068	-82.68	0.0704	75.02	24.0498	
3.4951	-102.97	0.2436	87.76	214.472	
3.8835				357.80	

Thus if one identifies the unit species of a crystal, the determination of the Phillips-Kleinman pseudopotential and the W potentials for the crystal reduces to a trivial job. The unit species can be easily selected from the knowledge of the unit cell. The forms of (11) are equivalent to a restatement for the crystalline case *that the crystal valence Fock operator mimicks the atomic valence Fock operator in the aggregate core region of space.*

As an example we consider a fictitious one-dimensional chain of sulphur atoms with spacing 2.06 Å. The sulphur atomic orbitals are chosen in a GTO basis set (table 1). Table 2 shows the different components of the crystal potential. In table 2 we have approximated W_c functions by direct coulomb repulsion although the W_v potentials have been calculated in an *ab initio* manner. The variation of crystal potentials along the coordinate axes are shown in figure 1. The sum of the nuclear attractive potential and the W potentials could have been compared with a Muffin-tin potential. However, the latter is often calculated by making reasonable approximations to the exchange term and of course empirically assuming constancy of the crystal potential in the interstitial region (Mattheiss 1964). In this work we refer to the construction of the W potentials in an *ab initio* fashion, although one may expect that the constancy would be approximately maintained. The distinction between *ab initio* effective potentials and empirical potentials has been well reviewed in literature (Ewig and VanWazer 1975 and related references). We further note that for an atom-centred (local) pseudo-orbital the Phillips-Kleinman term need not necessarily retain the full crystal symmetry.

The molecular assumption on the valence Fock operator is very fruitful since the atomic W potentials can be generated with a pre-determined basis set and directly transferred to different molecules. A similar procedure is applicable to different crystals provided the effective potential components are at first determined as func-

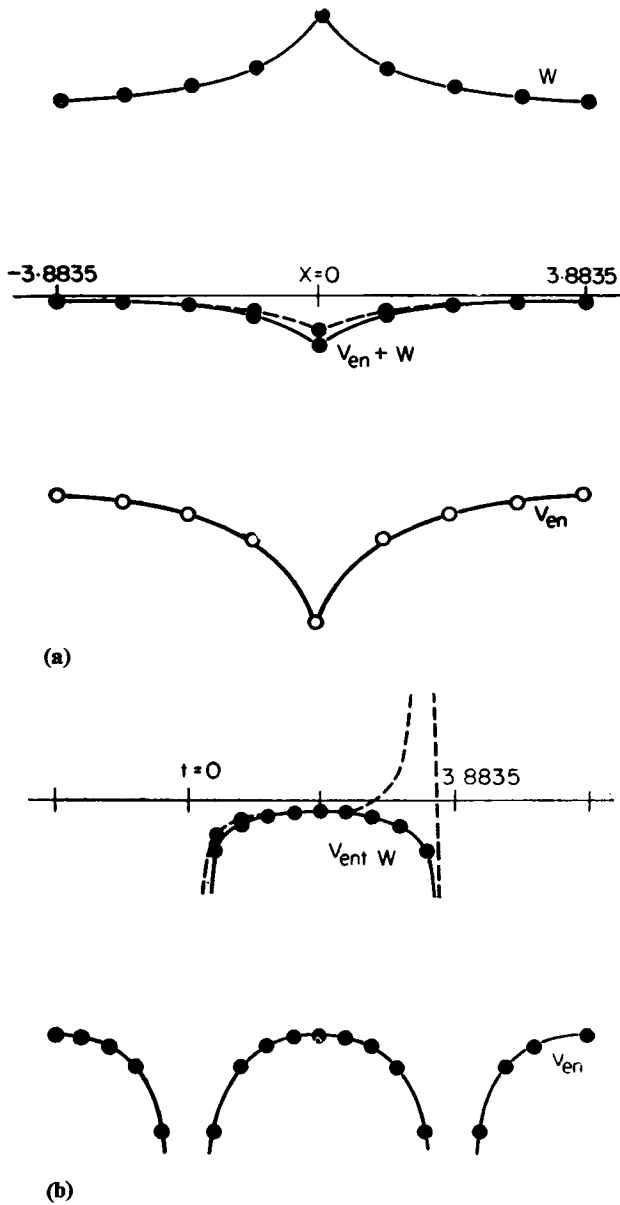


Figure 1. a. Variation of crystal potentials along the x -axis. b. Variation of crystal potential along the z -axis.

tions of interatomic distances and relative orientations and then evaluated as functions of lattice parameters.

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References

- Coffey P, Ewig C S and VanWazer J R 1975 *J. Am. Chem. Soc.* **97** 1656
Collins T C, Kunz A B and Deutsh P W 1974 *Phys. Rev.* **A10** 1034 (and reference therein)
Datta S N, Ewig C S and VanWazer J R 1978 *J. Mol. Struct.* **48** 407
Datta S N, Ewig C S and VanWazer J R 1978 *Chem. Phys. Lett.* **57** 83
Dagens L and Perrot F 1972 *Phys. Rev.* **B5** 641
Euwema R N, Wilhite D L and Surratt G T 1973 *Phys. Rev.* **B7** 818
Euwema R N, Surratt G T, Wilhite D L and Wepfer G G 1974 *Philos. Mag.* **29** 1033
Euwema R N, Surratt G T, Wilhite D L and Wepfer G G 1974 *Phys. Rev.* **B9** 5249
Ewig C S, Coffey P and VanWazer J R 1975 *Inorg. Chem.* **14** 1848
Ewig C S and VanWazer J R 1975 *J. Chem. Phys.* **63** 4035
Ewig C S, Osman R and VanWazer J R 1977 *J. Chem. Phys.* **66** 3557
Harris F E and Monkhorst H J 1969 *Phys. Rev. Lett.* **23** 1026
Kahn L R, and Goddard W A III 1972 *J. Chem. Phys.* **56** 2685
Kahn L R, Baybutt P and Truhlar D G 1976 *J. Chem. Phys.* **65** 3826
Kunz A B 1969 *Phys. Status. Solidi.* **36** 301
Kunz A B 1971 *Phys. Status. Solidi* **B46** 697
Kunz A B 1972 *Phys. Rev.* **B6** 606
Kunz A B, Mickish D J and Collins T C 1973 *Phys. Rev. Lett.* **31** 756
Mickish D J, Kunz A B and Collins T C 1974 *Phys. Rev.* **B9** 4461
Mattheiss L F 1964 *Phys. Rev.* **134** A970
Osman R, Coffey P and VanWazer J R 1976 *Inorg. Chem.* **15** 287
Phillips J C and Kleinman L 1959 *Phys. Rev.* **116** 287
Surratt G T, Euwema R N and Wilhite D L 1973 *Phys. Rev.* **B8** 4019