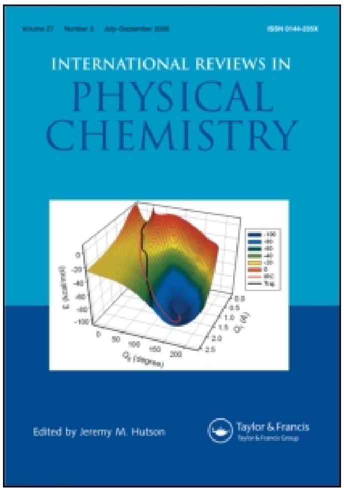

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Hartree-Fock *ab initio* approaches to the solution of some solid-state problems: state of the art and prospects

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Hartree–Fock *ab initio* approaches to the solution of some solid-state problems: state of the art and prospects

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The state of the art of Hartree–Fock (HF) computational schemes for use in solid-state physics is reviewed. Particular attention is devoted to the perfect crystal problem: the fundamental techniques are discussed, and the computational difficulties are presented. It is shown that present-day HF schemes compare favourably with those based on density functional theories in a number of instances; in particular, in the determination of the one-electron properties of covalent and ionic crystals which do not contain heavy atoms, and in the chemical and structural characterization of their surfaces. However, in order to find extensive application in solid-state physics, HF schemes need further development: the possible implementation of pseudopotential techniques, correlation corrections, and embedding schemes is discussed.

1. Introduction

There are a number of problems in solid-state physics where an accurate *ab initio* description of the ground state of the system and its properties are of primary importance.

The ground-state energy E_0 is usually the most interesting parameter. For perfect crystals, equilibrium geometry, elastic properties, relative stabilities of different crystal phases, etc. can be obtained from the knowledge of E_0 as a function of the coordinates of nuclei. More generally, E_0 may provide information about the surface energy of different crystal faces, about their relaxation or reconstruction, about the chemisorption heat and equilibrium configuration of adsorbed molecules, about the formation energy of different defects in otherwise perfect crystals. This information is valuable in the areas of material science and catalysis, especially in situations where experimental data are difficult to collect or have ambiguous interpretation. Ground-state electron properties such as electron charge and electron momentum distribution may clarify the nature of bonding in crystals. Semiempirical schemes may be parameterized with reference to those 'exact' results, and may then be used with some confidence for treating a number of systems which are beyond the reach of *ab initio* treatments.

Among the techniques that are currently available for the solution of the many-electron problem, the Hartree–Fock (HF) approach in its linearized Roothaan version appears in principle well suited for these kinds of problems, since it provides the single-determinant wavefunction with the lowest expectation value for energy within the functional space spanned by the adopted basis set. Decades of application of the HF approximation to molecular problems have resulted in the generation of extremely refined, relatively standard computer programs such as, for example, GAUSSIAN 82 (Binkley *et al.* 1981). A few well calibrated basis functions per involved atom are adopted, usually designed as atomic orbitals (AO), which are defined as a linear combination of a certain number of Gaussian type orbitals (GTO); well assessed strategies are available for selecting the optimal set as allowed by computational constraints (Davidson and Feller 1986); powerful algorithms have been developed for computing and handling all required one- and two-electron integrals (McMurchie and Davidson 1978). The correlation of electron motions is not taken into account in the HF approximation. A variety of techniques have been developed in the field of molecular studies for removing the 'correlation error' (Wilson 1984); for most of them, the calculation of the HF solution is a useful, if not necessary, step. The uncorrelated HF wavefunction is by itself a source of valuable information about molecular systems in their ground state. Equilibrium geometries, barriers to internal rotations, electron charge and momentum distributions are usually described with satisfactory accuracy.

For all these reasons, there has been in the past two decades strong stimulus to extending the use of the HF approximation to the investigation of the ground-state properties of solid systems. Molecular quantum chemistry programs have often been used for this purpose, especially in the study of defects, surfaces, and surface chemistry (see for instance Bauschlicher *et al.* (1975), Hermann and Bagus (1978), Colbourn and Mackrodt (1982), and Simonetta (1986)). In such calculations a small cluster of atoms from the solid is considered, whose configuration reproduces locally the crystal geometry; the rest of the system is often totally ignored, or simulated by saturating dangling bonds with hydrogen atoms or similar devices. Since the problem is reduced to a molecular one, sophisticated techniques can be applied for calculating correlation corrections (Beckmann and Koutecky 1982). The cluster technique has achieved some successes in describing local electronic features in solids. However, one cannot go very far this way: eliminating boundary and limited-size effects by simply increasing the number of atoms in the cluster is clearly a hopeless task.

The problem is simplified in an essential way in the case of perfect crystals, because advantage can be taken of translational symmetry. One first chooses a number of representative AOs $\chi_\mu(\mathbf{r})$ ($\mu = 1, \ldots, p$) associated with the atoms in the reference cell; by applying to each of them the projection operator $P(\mathbf{k})$ (the continuous label $\mathbf{k}$ specifies the general irreducible representation of the group of the crystal translations), Bloch functions (BF) $\phi_\mu(\mathbf{k};\mathbf{r})$ are generated. In the BF representation the Fock matrix $\mathbf{F}$ becomes block-diagonal, the order of each block along the diagonal, $\mathbf{F}(\mathbf{k})$, being p. The task of calculating the crystalline orbitals (CO) $\Psi_i(\mathbf{k})$, eigenfunctions of the Fock equations, is reduced to the simple problem of diagonalizing the 'small' matrices $\mathbf{F}(\mathbf{k})$. The main difficulties that are left in the calculation are evaluating the matrix elements $\mathbf{F}_{\mu\nu}(\mathbf{k})$, and sampling and interpolating with respect to the continuous $\mathbf{k}$ parameter.

Having at hand the HF solution for the translationally periodic system makes it possible, on the one hand, to exploit the related information for studying local defects in otherwise perfect crystals by means of suitable embedding techniques (see for instance Pisani (1986)) and on the other hand, to introduce corrective algorithms for removing or estimating the correlation error, especially concerning the ground-state energy E_0.

A realistic and attractive line of research can be formulated following these considerations. A crucial step for its realization is the implementation of a general purpose HF program for perfect crystals, characterized by a number of desirable features:

(*a*) it should resemble molecular programs in so far as functional form of the AOs and basic algorithms are concerned: efficient criteria for basis set selection, powerful numerical techniques, and useful interpretative schemes developed in the field of molecular quantum chemistry could then be utilized;

(*b*) it should allow the treatment of systems with one-, two-, or three-dimensional periodicity, and should not introduce too strict limitations as regards the complexity of the unit cell (up to ten atoms, say, should be allowed) and the nature of the atoms involved: the versatility of the program critically depends on the fulfilment of all these conditions;

(*c*) it should be sophisticated enough to exploit all possible means for reducing the computational effort, in particular by taking advantage of point symmetry; yet, its use should be easy, both concerning the definition of the system to be treated and of the computational parameters to be adopted, and the extraction of the relevant information from the results of the calculation.

In the past two decades there have been many attempts to achieve those aims. Section 2 gives a short account of the various HF approaches that have been proposed for the study of crystals, and of the main problems that have been encountered. In spite of the relevant successes that have occasionally been obtained, most of these efforts have not resulted in standard computational schemes. The main reason for that is probably the fact that in solid-state physics there exist highly efficient alternative routes for the solution of the many-electron problem. Section 3 briefly describes the state of the art in the field, with special attention given to those *ab initio* schemes that refer to density-functional (DF) theories. In their most sophisticated version, these approaches can provide detailed and reliable information on the ground-state properties of crystals. In spite of that, the HF 'chemical' approach to the study of solids remains an important option to be carefully explored, especially because its theoretical foundations are sounder and better understood than is the case with DF theories; however, in order to compete at a level of parity with well established DF theories, HF schemes must come close to meeting those requirements that have been listed above. Section 4 presents some aspects of the program CRYSTAL developed in this laboratory, which is at present the best tested HF program for periodic systems. With the help of some examples, current possibilities and critical aspects of this kind of approach are documented. Finally, Section 5 tries to delineate some directions of work in this area of research in the near future.

2. HF approaches to the study of perfect crystals

There is no unique way to formulate and to solve the HF–Roothaan equations for crystals. They are reduced to a trivial problem when a minimal set of generating AOs is adopted to describe approximately closed-shell atoms or ions in the crystal environment, that is, when the number of spin orbitals that can be constructed equals the number of electrons that must be accommodated. In this case no variational freedom may be left for the definition of the Slater determinant which approximates the ground-state wavefunction; the one-electron density matrix is simply the inverse overlap matrix and the ground-state one-electron properties and energy are hence obtained in a straightforward way. Such an approach is particularly useful with ionic systems, where several schemes have been used for choosing a suitable minimal set (Lundqvist 1954, Paakkari *et al.* 1976, Grosso and Pastori Parravicini 1979). In principle this method is exact for insulators if the generating AOs closely resemble the crystal's Wannier functions (see Callaway (1974), pp. 375–382). An elaborate procedure for determining the optimized minimal set while maintaining the localized character of the basis functions has been proposed and tested by Kunz with a number of ionic systems (Kunz 1970, Mickish *et al.* 1974 a, Pantelides *et al.* 1974, Kunz and Mickish

1975). Similar methods have been applied to other kinds of system, even metallic ones such as calcium (Mickish *et al.* 1974 b) or beryllium (Ludeña 1978), where the procedure is certainly less justified.

In general, however, one must allow for more or less large variational freedom and there is the need to define the manifold of the occupied COs according to a self-consistent procedure. The sequence of computational steps to be undertaken is as follows:

(*a*) Define the geometry, the nature of atoms, and the basis set.
(*b*) Evaluate and store auxiliary integrals.
(*c*) Define a trial density matrix $\mathbf{P}_0$.
(Begin loop over a selected set of $\mathbf{k}_i$ values.
(*d*) Calculate the Fock matrix $\mathbf{F}(\mathbf{k}_i)$ in the BF representation.
(*e*) Find eigenvalues $\mathbf{E}(\mathbf{k}_i)$ and eigenvectors $\mathbf{A}(\mathbf{k}_i)$ of the orthogonalized Fock matrix.
End loop over $\mathbf{k}_i$.)
(*f*) Calculate the new $\mathbf{P}_n$ matrix by an interpolation–integration process from the knowledge of the sampled values $\mathbf{E}(\mathbf{k})$, $\mathbf{A}(\mathbf{k})$.
(*g*) Check for convergence by comparing $\mathbf{P}_n$ with $\mathbf{P}_{n-1}$; if not reached, repeat all steps following step (*c*).

The step which more deeply characterizes a given computational scheme is probably step (*d*) above. For the evaluation of the general Fock matrix element $\mathbf{F}_{\mu\nu}(\mathbf{k})$, one must consider three contributions: the kinetic term, which is relatively straightforward, the Coulomb term, corresponding to the electrostatic interaction between the charge distribution $\phi_\mu^*(\mathbf{k};\mathbf{r})\,\phi_\nu(\mathbf{k};\mathbf{r})$ and all the charges in the crystal, both nuclear and electronic, and the exchange term, corresponding to a non-local operator typical of the HF approximation, which corrects the Coulomb term by accounting for the Fermi repulsion between electrons with the same spin. For performing these calculations, either a 'configuration space' (CS) or a 'momentum space' (MS) approach may be adopted.

In the former case, which is certainly the more popular, all integrals are performed in direct space and the Fock matrix is Fourier transformed to reciprocal space just before diagonalization. The explicit reformulation of the HF–Roothaan equations in a basis set of BFs and adopting a CS approach is due to Del Re *et al.* (1967), and to André *et al.* (1967). The Coulomb and exchange terms are expressed as a triple summation over all the crystal cells, and the problem arises of truncating these infinite series in an efficient way (see section 4 for more details). A very large number of one- and two-electron integrals are to be calculated involving AOs on different crystal cells: they can be evaluated and stored once and for all in a preliminary step of the calculation (step (*b*) of the scheme above).

If an MS approach is adopted, the Fock matrix is calculated analytically in reciprocal space after expressing both BFs and Coulomb and exchange operators as a combination of plane waves (see for example Harris and Monkhorst (1970), Stoll and Preuss (1975), Brener and Fry (1978), and Delhalle and Harris (1985)). In spite of the elegance of the MS approach, it has had only very limited application. It has been claimed (Delhalle and Harris 1985) that MS approaches are superior in principle to CS ones because the quantity of information to be stored for use in the self-consistent stage of the computation is much larger in the latter case. However, it can be shown that an adequate treatment of the problem can reduce all storage requirements to much more manageable proportions than would appear necessary at first sight. Furthermore, with CS approaches, it is much easier to embody in the computational scheme powerful numerical techniques developed in molecular quantum chemistry.

The progress towards the implementation of such self-consistent HF schemes has been quite rapid in the case of ideal polymers, that is of one-dimensional periodic systems (see the review by Kertész (1983) for a detailed account of techniques and results), where the problem is somewhat similar to the molecular one. Powerful computer programs and accurate HF solutions for a number of polymers are available, mainly due to extensive work by several research groups (Kertész *et al.* 1977, Brédas *et al.* 1978, André 1980, Suhai 1980, Karpfen 1981, 1982).

With three-dimensional systems the problem is much more delicate. First of all, the truncation of the Coulomb and exchange series cannot be based only on a criterion of distance between the centres of the AOs, because the number of integrals increases very rapidly with the truncation radius while the value of the individual terms is decreasing only with the inverse radius. Second, the full exploitation of point symmetry is here both more important and more difficult to achieve. Third, for calculating the Fermi energy in metallic systems, and more generally for reconstructing the Fock matrix at different **k** points, sophisticated interpolation–integration techniques must be adopted for three-dimensional structures, while the problem is trivial in one dimension.

The first successful attempt to solve directly the HF–Roothaan equations for three-dimensional systems in a CS approach, by coping with all the fundamental difficulties mentioned above, is due to the research group of the Aerospace Research Laboratories, Dayton, Ohio. They used a set of contracted lobe Gaussian functions and employed sophisticated techniques including full exploitation of crystal symmetry for reducing to a minimum the number of integrals to be computed. Their studies of diamond (Euwema *et al.* 1973, Surratt *et al.* 1973, Wepfer *et al.* 1974, Euwema and Greene 1975), cubic boron nitride (Euwema *et al.* 1974 a), lithium fluoride (Euwema *et al.* 1974 b) have remained for many years an unsurpassed standard in the field of HF studies of crystals. The energy bands of diamond and LiF have subsequently been corrected by Brener (1975 a, b) by approximately taking into account correlation effects.

A number of research groups have undertaken in recent years similar attempts. Stoll and Preuss (1973, 1975) have applied their MS scheme based on the use of modulated periodic functions (a sum of AOs over the crystal cells multiplied by a modulating plane wave) to the study of lithium and beryllium. Harris, Monkhorst and co-workers (Harris and Monkhorst 1969, 1970, Harris *et al.* 1973, Graovac *et al.* 1975, Ramaker *et al.* 1975, Monkhorst *et al.* 1979, Pack *et al.* 1979) have produced fundamental work, primarily methodological in character (the only application concerns metallic hydrogen and lithium), intended to explore and discuss the theoretical and computational aspects of the MS approach to the HF problem for crystals. A different MS scheme has been applied by Mauger and Lannoo (1977) to the study of diamond. In the same years, Brener and Fry (Fry *et al.* 1977, Brener and Fry 1978) developed powerful algorithms for the treatment of the exchange series in a MS formalism. Upton and Goddard (1980) have developed a CS scheme with special attention to the treatment of Coulomb sums and tested it with metallic hydrogen, lithium and sodium. Von der Linden *et al.* (1986) have proposed a technique for eliminating the exchange problem in the self consistent part of the calculation by using the COs from a local-density-functional treatment of the problem for calculating the nonlocal HF exchange potential; preliminary applications concern diamond and silicon.

The scheme to be presented in some detail in section 4 has been developed at the Institute of Theoretical Chemistry of the University of Turin, and by Saunders, of the Daresbury Laboratories (Pisani and Dovesi 1980, Dovesi *et al.* 1983 a, Dovesi 1986, Causà *et al.* 1987 a). In comparison with those mentioned above, this scheme does not present essential methodological differences and is near in spirit and methods to Euwema's approach. However, the corresponding computer program, which has been named CRYSTAL, is the only one that has been systematically improved over nearly ten years, and has been tested with a large variety of systems: the graphite monolayer, both bare (Dovesi *et al.* 1980 a) and covered with chemisorbed hydrogen (Dovesi *et al.* 1981 a); diamond (Dovesi *et al.* 1980 b); silicon (Dovesi *et al.* 1981 b, Angonoa *et al.* 1981); hexagonal and cubic boron nitride (Dovesi *et al.* 1981 c); aluminum (Causà *et al.* 1981); beryllium (Dovesi *et al.* 1982 a, b, c); beryllium slabs, both bare (Angonoa *et al.* 1982) and covered with chemisorbed hydrogen (Angonoa *et al.* 1984 a); lithium (Dovesi *et al.* 1983 b); polyacetylenes (Dovesi 1984); polysulphur nitride (Dovesi *et al.* 1984 a); lithium hydride (Dovesi *et al.* 1984 b); lithium nitride (Dovesi *et al.* 1984 c, Causà *et al.* 1985); lithium oxide (Dovesi 1985); magnesium oxide (Causà *et al.* 1986 a, b, c); the (100) surface of magnesium oxide (Causà *et al.* 1986 d). The list includes non-conductors and semiconductors, metals, ionic systems, two-dimensional structures (layered compounds, crystal surfaces bare or covered with adlayers), and polymers.

3. The alternative choice: *ab initio* density functional calculations

In spite of all these efforts, HF approaches have not yet gained great relevance in solid-state physics. The overwhelming majority of the calculations aimed at describing the electronic structure of periodic systems is currently performed using DF theories. There are both fundamental and historical reasons for that. It has been standard practice for a long time to investigate the electronic properties of solids (in particular their response properties) by employing semi-empirical one-electron hamiltonians, suitably parametrized for any given specific problem. The DF theory (Hohenberg and Kohn 1964, Kohn and Sham 1965) has provided firm ground for formulating an effective potential $w(\mathbf{r})$ to be added to the kinetic operator and to the Coulomb potential: in principle $w(\mathbf{r})$ is a universal functional of the electron charge density $\rho(\mathbf{r}')$ such that the COs that are calculated with its use following a self-consistent procedure generate the true charge density of the system in its ground state, $\rho_0(\mathbf{r}')$; in turn, all observable ground-state quantities (in particular E_0) are functionals of ρ_0. Explicit formulae can be obtained for all the functionals in the limit of nearly uniform charge density, starting from the properties of the uniform electron gas. This form of the theory corresponds to the 'local approximation'; in this case, the effective potential w at a specific point $\mathbf{r}$ depends only on the density at that point.

This theory has had enormous fortune in solid-state physics, much less so in molecular quantum chemistry (Dahl and Avery 1984). The local effective potential includes both exchange and correlation effects, and is easily fitted into traditional computational schemes of solid-state physics; with the constant progress in numerical techniques, and with the parallel definition of better and better effective potentials, these schemes have now assumed a first-principles (*ab initio*) parameter-free form. Techniques originated from the electron-gas model, such as the muffin-tin augmented-plane-wave scheme, are now extended to include any shape of the periodic potential in the crystal (Andersen 1975, Wimmer *et al.* 1981, Blaha *et al.* 1985). In turn, the tight-binding approximation has been improved by increasing the number of AOs used as a basis set, and by progressively removing all empirical parameters from the theory

(Heaton and Lafon 1978, Vanderbilt and Louie 1984). Very often, the calculation is restricted to valence electrons by adopting a frozen-core approximation; suitable pseudopotentials are then added to account for core electron charge and to prevent valence electrons from occupying core states. This choice is nearly mandatory when plane waves (PW) are adopted as a basis set, because an enormous number of PWs would be required for describing the sharp features associated with core electrons. As an example of such an approach, let us consider the PW soft-core-pseudopotential local-DF MS scheme of Cohen and co-workers (Cohen 1981, Yin and Cohen 1982); it is at the same time one of the most successful *ab initio* schemes that are current in solid-state physics, and one that is most different from an LCAO all-electron HF CS approach to the problem of solids. PWs form a universal, orthonormal set, with the correct asymptotic behaviour; with them, a MS approach is the natural choice: all matrix elements of the hamiltonian are calculated in a straightforward way after performing a Fourier transform of the valence charge density, of the exchange-correlation effective potential, and of the core pseudopotential (Yin and Cohen 1982). The scheme has been applied to a number of systems including metals (Chou *et al.* 1983), semiconductors (Chang and Cohen 1985), ionic systems (Chang and Cohen 1984), and two-dimensional structures treated with the multislab technique (Northrup and Cohen 1984). This extremely general procedure may meet difficulties when systems are treated whose elementary cell contains many atoms and/or regions of very low electron density, since the number of PWs required to describe valence electrons might then become very large.

The existence of such powerful, sophisticated and versatile schemes, able to provide detailed and reliable information on the ground-state properties of a large variety of crystalline systems, makes it difficult for cumbersome HF schemes, intrinsically affected by the correlation error, to find popularity among solid-state physicists. On the other hand, local density approaches cannot be improved indefinitely without a deep revision of their fundamental assumptions and related algorithms. The inadequacies of local density approximations, essentially due to the different nodal structures of the different orbitals, have been discussed by Gunnarsson and Jones (1985). According to their discussion it would not seem easy to overcome these problems by simple nonlocal modifications of local DF theories. As they state it: 'the problem represents a challenge for both solid state and molecular physicists'. Among the recent attempts to improve upon existing local DF theories, the schemes developed by Langreth, Mehl and Perdew can be mentioned (Langreth and Perdew 1980, Langreth and Mehl 1983, 1984, Perdew and Yue 1986, Perdew 1986), based on a description of exchange and correlation in reciprocal space. The HF hamiltonian does not suffer from these kinds of problem because the corresponding single-determinantal wavefunction is a clearly defined quantity that takes into account the different nodal structures of the different orbitals through its nonlocal exchange term.

4. Present capabilities and open problems of HF computational schemes

A schematic account of the general characteristics, capabilities, and open problems of the HF CRYSTAL program (see section 2) may clarify the present position of HF approaches with respect to DF ones.

4.1. *Basis set problems*

The problem of selecting appropriate basis functions for HF calculations of crystals has many features in common with the corresponding one for molecules; yet, some aspects are markedly different. Diffuse Gaussian orbitals (exponent coefficient of the order of 0·2 a.u. or less), play a critical role in HF CS calculations of crystals. The number of integrals to be explicitly calculated increases dramatically with decreasing exponent; this effect is absent in molecular calculations. Furthermore, with decreasing exponent, the risks of pseudo-linear dependence increase rapidly; in practice, it is sometimes impossible to reach a variationally optimized basis set before a numerical catastrophe occurs (see for example Dovesi *et al.* (1983 b)). On the other hand, very diffuse AOs are less important in three-dimensional densely packed crystals than in atoms and molecules, where they serve to describe the tails of the electronic distribution towards vacuum (Euwema *et al.* 1973); the need for diffuse functions is clearly of greater importance in calculations of two-dimensional structures and of polymers. For these reasons, the selection of appropriate basis sets must be performed following specific rules for each crystal structure. Accurate basis sets for the treatment of a number of atomic or ionic species in their ordinary crystalline environments (Li^+, Be, Mg^{2+}, N^{3-}, O^{2-}) are provided in the series of papers by Dovesi *et al.* and Causà *et al.* quoted in section 2, but much work is still required before a rich library of reference basis sets for HF computations of solids are available. When crystals with many atoms per unit cell are to be treated, relatively poor basis sets must be used, such as the STO-3G sets proposed by Pople and co-workers for HF molecular calculations (Hehre *et al.* 1969, 1970, Pietro *et al.* 1980, 1981). In such cases, problems may arise when an estimate of the HF binding energy is desired, which is obtained by subtracting the total crystal energy per molecular unit from the sum of the HF energies of the isolated atoms. The latter should be calculated at the same level of accuracy. Using, however, the same AOs for the isolated atoms as in the crystal leads to an overestimation of the HF binding energy, since the variational freedom is actually larger in the crystal because valence orbitals are shared by a large number of neighbouring atoms. This is known in quantum chemistry as basis set superposition error. In order to correct it, the counterpoise method (Boys and Bernardi 1970) may be used: the reference atomic energy is obtained using all AOs of that atom supplemented by the valence AOs of the surrounding atoms.

4.2. *Treatment of Coulomb interactions*

For the evaluation of the Coulomb contributions to the total energy and Fock matrix in crystals, proper coupling of electron–nucleus and electron–electron interactions is essential. For this purpose, the technique proposed by Dovesi *et al.* (1983 a) may be adopted. It may be described as follows, with reference to the general element F_{12} of the Fock matrix in direct space. The Coulomb contribution F_{12}^{C} to that element is the electrostatic interaction of the charge distribution $\rho_{12}(\mathbf{r})$ (corresponding to the product $\chi_1(\mathbf{r})\chi_2(\mathbf{r})$ of two AOs of which the former is in the zero reference cell) with all electrons and nuclei in the crystal. One first classifies all shells λ of AOs on all atoms in the crystal in two categories, λ' and λ'', according to whether they overlap appreciably or not with ρ_{12}. For the relatively few λ' shells, the Coulomb interaction is calculated exactly. For all the others, it is calculated approximately after adding the corresponding nuclear charges (which exactly compensate electron charges in each crystal cell), by considering a truncated multipole expansion and adopting Ewald techniques for summing to infinity. The exact part of the Coulomb contribution:

$$F_{12}^{C,\text{exact}} = \sum_{3\in\lambda'}\sum_{4} P_{34}\,(\chi_1\chi_2|\chi_3\chi_4)$$

requires in principle the evaluation of an infinite number of bielectronic integrals; however, only those are actually calculated for which the absolute value of the overlap of χ_1 with χ_2 and of χ_3 with χ_4 is above a certain threshold S^C.

4.3. *Treatment of exchange interactions*

The exchange series does not require special manipulations of the kind discussed above for the Coulomb series; rather, a careful selection of terms that appreciably contribute to the Fock matrix and to the total energy is needed. In a CS HF approach the general exchange contribution to total energy is of the form:

$$-(1/4)P_{12}P_{34}(\chi_1\chi_3|\chi_2\chi_4)$$

The simplest truncation criterion that can be adopted is based on two parameters: S^{ex}, a threshold for the overlap between the AOs χ_1 and χ_3 or between χ_2 and χ_4, and R^{ex}, 'range of the density matrix' corresponding to a cutoff distance between the centres of AOs χ_1 and χ_2, or χ_3 and χ_4. A detailed study of the speed of convergence of the series with respect to these parameters (Causà *et al.* 1987 a) has led to the following conclusions. A value of S^{ex} of about 10^{-3} is normally sufficient for a numerical accuracy of 0·001 eV in total energy; lowering S^{ex} rapidly increases the accuracy, but also the number of required integrals. Convergence with respect to R^{ex} is much slower if small gap semiconductors or conductors are considered. If very accurate energy evaluations are needed the number of exchange integrals may become huge (hundreds of millions, say). If a moderate accuracy in total energy (0·03 eV/cell) is deemed sufficient, relatively small values of R^{ex} can be adopted, for example 4, 5, and 6 Å for MgO, silicon and aluminum, respectively; the latter calculation corresponds to about 6 million exchange integrals with a minimal basis set. When more accurate calculations are required, the large majority of exchange integrals concerns the interaction between charge distributions $\chi_1\chi_3$ and $\chi_2\chi_4$ which are far apart from each other and may be calculated accurately and economically using a multipolar expansion of the two distributions.

4.4. *Sampling and integration in reciprocal space*

The integration of **k**-dependent quantities is an important aspect of *ab initio* calculations for crystals. The problem arises at each stage of the self consistent procedure, when determining the Fermi energy and reconstructing the one-electron density matrix, and, after self consistency is reached, when calculating the density of states (DOS) and a number of observable quantities. Since the cost of evaluating the integrand at any given **k** point is usually high, it is important to maximize the exploitation of available information. This problem has no counterpart in ordinary molecular quantum chemistry where eigenvalues and eigenvectors corresponding to occupied molecular orbitals form a finite manifold, and it is possible to sum over all of them. Among the large variety of schemes that can be adopted (see for instance Boon *et al.* (1986)), the one adopted in CRYSTAL (Augonoa *et al.* 1984 b) is based on a truncated expansion in Legendre polynomials of the density of states as a function of energy; the coefficients of the expansion are estimated from the knowledge of the solution at a certain number $N_{\mathbf{k}}$ of properly selected **k** points, inequivalent by symmetry; all subsequent integrations are performed analytically. The whole procedure is extremely rapid. Its precision depends on the number $N_{\mathbf{k}}$ of sampling **k** points; in turn, the cost of the self-consistent part of the computation is proportional to $N_{\mathbf{k}}$. The density of sampling points in **k** space must be much higher for conductors (where there is the problem of an accurate determination of the Fermi surface). Typical values of N_k are 145 for metallic lithium, and 8 for magnesium oxide for comparable accuracy.

4.5. *Exploitation of point symmetry*

In all periodic calculations, point symmetry is exploited for reducing the number N_k of points in which the matrix equations are to be solved; in addition, a very extensive use of point symmetry is possible in HF LCAO SC schemes. In this case, 2-electron and 1-electron integrals are evaluated once and for all at the beginning of the calculation, and then used at each cycle of the self consistent procedure. The problem of the 'calculation and manipulation of horrendous numbers of many center integrals' (Monkhorst 1979) can be drastically simplified by the use of point symmetry: saving factors as large as h and h^2 (h is the order of the point group) can be obtained in the number of 2-electrons integrals to be computed and stored for the SCF part of the calculation, respectively. The main steps of the scheme that can be adopted (Dovesi 1986) for obtaining this result can be summarized as follows:

(i) The set of Coulomb and exchange integrals whose 3, 4 indices identify translationally equivalent pairs of AOs, so that the associated element of the density matrix P_{34} is the same, are summed together just after they have been computed, to give D_{1234} elements whose 1 and 3 indices are in the reference cell.

(ii) The products of AOs $\chi_1\chi_2$ (and $\chi_3\chi_4$) are classified in symmetry-related sets; using the fact that the Fock matrix is totally symmetric, only those D quantities are evaluated whose first indices 1, 2 refer to the first member of a symmetry set. The corresponding saving factor in CPU time and storage can be as large as h.

(iii) Using the symmetry properties of the density matrix, D quantities referring to 3, 4 couples belonging to the same symmetry set (and with the same 1, 2 index) can be combined after multiplication by appropriate symmetry matrices, so that a single quantity for each 3, 4 symmetry set is to be stored, with a further saving factor in storage of the order of h.

Similar arguments apply to the other integrals appearing in the Fock matrix and in the energy expression.

4.6. *Examples of application*

The table provides examples of 'extreme' and 'normal' applications of the CRYSTAL program.

The diamond calculation has been performed while trying to get as close as possible to the HF limit for subsequent application of correlation corrections (see the next section); the basis set quality and the numerical accuracy have therefore been carried to the maximum allowed refinement. The number of two-electron integrals that need be calculated is enormous because of the computational conditions; on the other hand, use of the rich point symmetry reduces to manageable proportions the number N' of symmetrized D sums to be stored (the overall saving factor is about 80). The computer time required for the self consistent calculation is negligible with respect to integral evaluation.

The polysulphur nitride calculation refers to current work intended to explore the importance of interchain interactions in crystalline conducting polymers. According to

Examples of application of the CRYSTAL program. The meaning of S^C, S^{ex} and R^{ex} is explained in the text. N^C, N^{ex} and N' are the number of two-electron Coulomb and exchange integrals, and of symmetrized D sums, respectively. The computation times refer to a Hitachi M200 scalar computer.

	Diamond	$3-d$ $(SN)_x$	MgO
Order of point group	48	4	48
Number of atoms per cell	2	8	2
Basis set	Optimized double-zeta $+d$ AOs	STO-3G $+d$ AOs on sulphur	Optimized split-valence
Number of AOs per cell	30	76	18
Computational parameters			
$S^{ex}=S^C$	10^{-6}	10^{-5}	10^{-4}
R^{ex} (A)	6·9	5·8	5·8
Order of multipoles	4	4	4
Calculation data			
Part I (evaluation of integrals)			
Number of integrals (millions)			
N^C	160	14	7
N^{ex}	150	19	5
N'	4	12	0·2
Computing time (s)	5500	1200	250
Part II (self consistent stage)			
$N_{\mathbf{k}}$ (sampling **k** points)	29	12	8
Number of SCF cycles	14	9	10
Computing time (s)	200	600	20

present standards it is again an extreme calculation, but in a different sense with respect to the preceding one: there are many atoms in the unit cell, some of them are second-row ones, the point symmetry is poor. A minimal STO-3G set has been employed, supplemented by d-type AOs on sulphur for describing important hypervalent aspects of the chemical bonds. In spite of the use of few sampling **k** points, the self consistent stage takes an appreciable fraction of overall computer time because of the large order (76), of the **F(k)** matrices.

Magnesium oxide corresponds to a ‘normal’ calculation of good quality (Causà *et al.* 1986 a). An optimized split-valence set is used which gives a total energy near the HF limit; however, the number of two-electron integrals is not very large because the AOs are relatively short-ranged. Furthermore, because of the rich point symmetry, there are only 200 000 symmetrized D sums to be stored and manipulated. The whole calculation takes only 5 min on a scalar computer.

4.7. *Concluding remarks*

After reaching self-consistency, a number of important quantities apart from E_0 may be obtained from the HF wavefunction. The following ones are available as a standard option of the CRYSTAL program:

(*a*) Mulliken charges and bond populations. These non-observable quantities are useful for a chemical characterization of the system, and for comparing different crystalline environments of a given species (see for example Dovesi *et al.* (1984 c)).

(*b*) Band structure. Even if HF band structures do not reproduce quantitatively the spectrum of one-electron excitations, they are usually topologically correct (see section 5 below); they may serve, for instance, for understanding the reactivity of crystal surfaces (Angonoa *et al.* 1984 a).

(*c*) Charge density and structure factors. Charge density maps, especially *difference* maps, provide further insight into the characteristics of chemical bonds in crystals (see for example Causà *et al.* (1986 d)). The Fourier transform of the charge density is comparable with the set of experimental X-ray structure factors; the good quality of the calculated charge density can thus be verified (Causà *et al.* 1986 b).

(*d*) Electron momentum density (EMD), Compton profiles (CP), autocorrelation function. EMD data reveal important aspects of the electronic structure in solids (Dovesi *et al.* 1983 b, Causà *et al.* 1986 d); CPs and autocorrelation functions are easily derived from this primary quantity, and may be compared with experiment: again, very good agreement is usually found (Causà *et al.* 1985).

The preceding analysis shows that sophisticated procedures for the HF treatment of crystalline solids are available. The range of application of a program like CRYSTAL is essentially limited by the number and type of the required basis functions. The present practicable upper bound is about one hundred AOs per unit cell in the most favourable case, that is, when AOs of small spatial extent may be used. Within such limits there are a number of interesting problems open to useful investigation. The quality of the results may compare favourably with those obtainable via DF approaches in many cases, such as for instance:

— determination of the one-electron properties of ionic and covalent crystals with moderately complex unit cells not containing heavy atoms;

— study of different crystal faces of these crystals by means of the thin-film model (an important class of problems here is the determination of equilibrium conformations; the availability of a technique for analytically calculating the energy gradient with respect to nuclear coordinates would be valuable for this purpose);

— study of polymeric systems, modelled by isolated infinite chains or by ordered arrays of parallel chains (Dovesi *et al.* 1984 c).

5. Prospective work

Much work is being devoted to a 'natural' extension of the capabilities of HF programs for crystals (refinement of algorithms, inclusion of analytic gradients, greater ease of use). Apart from that, a few directions of useful research activity may be indicated.

5.1. *Pseudopotential techniques*

Restricting the calculation to valence electrons impairs in principle the quality of the results. All-electron calculations provide direct information on core relaxation induced by the crystalline field (Dovesi *et al.* 1982 b), on the shift of core levels, etc., and may become necessary if one is interested in electronic and structural changes occurring in the system under very high pressures (Causà *et al.* 1986 a). On the other hand, getting rid of core electrons by the use of suitable pseudopotentials (PP) greatly increases the capabilities of the program when heavy atoms are considered. In the present context, we are specially interested in PPs designed for HF calculations, such as the 'non-empirical' PPs by the Toulouse group (Durand and Barthelat 1975, Barthelat *et al.* 1977), or the HF 'effective core potentials' recently tabulated by Hay and Wadt (Hay and Wadt 1985 a, b, Wadt and Hay 1985). Until now, HF PPs have only been tested in molecular calculations. They have been shown to provide accurate results comparable to all-electron calculations for a small fraction of the computational cost (the cost of a molecular calculation is roughly proportional to N^4, N being the number of basis functions included in the actual computation). The use of PPs in LCAO-HF calculations for crystalline systems is not expected to provide cost-saving factors as favourable as for molecules. Due to the truncation schemes that can be adopted (see section 4), the number of two-electron integrals that need be calculated is roughly proportional to $(N_v^4 + N_c N_v^3)$ rather than to $(N_c + N_v)^4$, N_c and N_v being the number of core and valence AOs, respectively. The advantage may still be considerable, especially in the SCF stage where matrices of order N_v instead of $(N_v + N_c)$ are to be constructed and manipulated. Modifying an all-electron crystalline HF program that employs GTOs as primitive basis functions, for the inclusion of PPs of the kind mentioned above is relatively straightforward. No new types of integrals appear and only the expressions for Fock matrix elements and total energy must be changed. On the other hand, it is know that PPs perform best when the valence orbitals used for the molecular (or crystalline) calculation are precisely the pseudo-valence orbitals which have served for their generation. But as discussed in section 4, AOs which are suitable for describing the isolated atom, or the atom in an ordinary molecular environment, are usually not suited for crystalline calculations. Essentially, less diffuse AOs must be used, and their definition is specific for each crystalline environment; the question is open whether standard PP expressions can safely be used in spite of this problem.

5.2. *Correlation corrections*

We have shown that the usefulness of HF approaches could be greatly increased by the introduction of correlation corrections. Extending to HF calculations for solids the methods and ideas developed for this purpose in molecular studies (see for instance Wilson (1984)) is not an easy task. In particular, configuration interaction techniques are not directly transferable to infinite systems because they do not satisfy the requirement of 'size-consistency', that is, the corresponding expression for the correlation energy is not asymptotically proportional to the number N of electrons in the system. A number of schemes are currently explored, and it is not yet clear which of them is preferable, also because of the fact that good HF wavefunctions for crystals have only recently become available.

The most natural way to deal with the correlation problem for solids is the intrinsically size-consistent Green's function method (Hedin and Lundqvist 1969). Knowledge of the one-electron Green's function (or equivalently, of the self-energy kernel) provides the correct ground-state energy of the system, its one-particle excitation spectrum (band structure), and its first-order density matrix. In principle, it is well known how to express the self-energy in terms of HF eigenvalues and eigenvectors, for example as a diagrammatic series. Methods for exactly treating the series to finite order and approximately to infinite order for molecular applications have been reviewed by von Niessen *et al.* (1984). When trying to apply these methods to crystals, computational difficulties arise. First, one must transform the two-electron integrals from an AO to a CO representation, which may be very cumbersome; second, when calculating the various diagrammatic contributions to the self-energy, multiple summations over the CO indices must be performed, which entails the need for multiple integration over the continuous **k** index (three such integrations for second-order diagrams, four in third-order, etc). For both problems, the availability of simple techniques for **k** space integrations seems critically important. Liegener (1985) has provided an example of rigorous application of such techniques, by treating to third order in the diagrammatic series the infinite alternating chain of hydrogen atoms. These kinds of treatment are closely related to the Møller–Plesset perturbative scheme, which considers the full hamiltonian as a perturbed HF hamiltonian. Suhai (1983) has recently demonstrated the usefulness of this scheme in one-dimensional periodic calculations, by correcting the HF band structure of trans-polyacetylene through the inclusion of all significant matrix elements to second order.

It is more customary in solid-state physics to adopt approximate expressions for the self-energy, not based on a truncation of the infinite perturbative series but on physically sound assumptions; the HF wavefunction is there used essentially for defining the one-electron density matrix and derived quantities. Among these kinds of approximation, we can mention the so called 'Coulomb hole plus screened exchange (COHSEX)' approximation which has found widespread use for correcting the HF band structure of semiconductors and insulators (Lipari and Fowler 1970, Brener 1975 a, b, Strinati *et al.* 1982, Baroni *et al.* 1985). It is interesting to note that this correction does not alter in any essential way the topology of the HF band structure, its main effects being a reduction of valence bandwidths, and a shift of conduction bands downwards, and of valence bands upwards, toward the Fermi level.

Another size-consistent scheme for the treatment of correlation effects which is being introduced in solid-state theory is the coupled cluster approximation (see for instance Pàldus *et al.* (1984)). A similar approach, relying on the use of appropriately chosen local functions to which the pair-excitation operators are applied, has been followed by Fulde and co-workers for treating electron correlations in insulators and semiconductors (Kiel *et al.* 1982, Horsch *et al.* 1983, 1984, Borrmann and Fulde 1985).

For all those problems where the main parameter of interest is the ground-state energy E_0, a simple means for evaluating the correlation energy would be valuable. The HF one-electron density matrix is known to be a good approximation to the exact one, except in some critical cases. Density functionals developed in the framework of DF theories can therefore be utilized with reference to HF densities. The correlation-only functional proposed by Perdew and Yue (Perdew and Yue 1986, Perdew 1986) and obtained from a generalized gradient expansion appears particularly promising in this respect. Its application to atoms and ions, using HF densities as input data, gives impressively good results from hydrogen to argon. The nonlocal DF formulated by Colle and Slavetti (1975, 1979, 1983) for evaluating the correlation energy of molecular systems has many features in common with the Perdew functional, but has been derived in a different theoretical framework, that is, starting from an ansatz concerning the expression of the correlated wavefunction. One of its attractive features is that it is intrinsically free from the self-interaction term, that is, it provides no correlation energy for one-electron systems. Preliminary tests of applications of the Colle–Salvetti functional in periodic systems are being performed; they provide generally good results except for metallic systems.

5.3. *Embedding techniques*

Having solved the HF problem for a perfect crystal, it would be worthwhile to exploit the related information in the study of point-defect problems. One could be interested for example in characterizing a chemical impurity or a vacancy in an otherwise perfect crystal by determining the energy of formation of the defect, the position of the impurity levels (if any), the spatial extent of the associated states; or else, one could want to investigate the reactivity properties of a certain crystal face (the reference 'perfect crystal' is here a thin periodic film), by calculating the equilibrium geometries and chemisorption energies of different adspecies. Since the perturbation is quite localized in these cases, the actual calculation may be restricted to a small region C surrounding the defect, by imposing the local solution to match with the extended crystal states at the boundary of C. Embedding techniques provide the means to do that (for a review up to 1978 see Pantelides (1978)). By far the most widely used approach is the Green's function technique originally proposed by Koster and Slater (1954). Here C is chosen to coincide with the region where the perturbation V is different from zero, and the Green matrix G_C in that region is obtained in terms of the Green matrix G_C^f of the host crystal by solving the Dyson equation. Other interesting approaches have been proposed; for instance, Inglesfield (Inglesfield 1981, Baraff and Schlüter 1986) defines an embedding potential, different from zero only at the surface of the defect region, which ensures the regular behaviour of the wavefunction across the boundary; Whitten (Whitten and Pakkanen 1980, Cremaschi and Whitten 1981) suggests exploiting the SCF solution of the host crystal (or of a large cluster that mimics the host crystal) for obtaining, through a unitary transformation, localized functions to be used for an accurate calculation in the defect region; Pisani (Pisani 1978, 1986, Pisani *et al.* 1979) shows how to correct the Green function of the isolated cluster by means of suitable energy-dependent coupling matrices that can be obtained from the host crystal solution.

The majority of the embedding calculations use relatively crude models for describing the host crystal and the defect region. In recent years, however, the trend has been toward more and more accurate hamiltonians and adequate basis sets. The time is ripe for a fully self-consistent HF treatment of simple defects in crystals by one or another of the embedding approaches just mentioned. Such a level of description is probably sufficient to reveal all the important chemical features of the defect problem; the correlation contribution to the defect formation energy could be estimated *a posteriori* by using, for instance, the Colle and Salvetti (1983) density functional.

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