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Space group symmetry applied to SCF calculations with periodic boundary conditions and Gaussian orbitals

by

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ABSTRACT

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We report theoretical, algorithmic, and computational aspects of exploiting space-group symmetry in self-consistent field (SCF) calculations, primarily Kohn–Sham density functional theory (DFT), with periodic boundary conditions (PBC) and Gaussian-type orbitals. Incorporating exact exchange leads to generally better performance for a broad class of systems, but leads to a significant increase of computation time, especially for 3D solids, due to a large number of explicitly evaluated two-electron integrals. We exploit reduction of the list thereof based on the space-group symmetry of a crystal. As distinct from previous achievements, based on the use of symmorphic groups only, we extend our technique to non-symmorphic groups, thus enabling application of any of 230 3D space groups. Algorithms facilitating efficient reduction of the list of two-electron integrals and restoring the full Fock-type matrix have been proposed and implemented in the development version of Gaussian program. These schemes are applied not only to the HFx, but also to explicit evaluation of the near-field Coulomb contribution. In 3D solids with smallest unit cells speedup factors range from 2X to 9X for the near field Coulomb part and from 3X to 8X for the exact exchange, thus leading to a substantial reduction of the overall computational cost. Factors noticeably lower than the number of the operations are due to
the highly symmetric atomic positions in crystals, as well as to the choice of primitive cells. In systems with atoms on general positions or in special positions of low multiplicity, the speedup factors readily exceed one order of magnitude being almost 70X (near-field Coulomb) and 57X (HFx) for the largest tested (16,7) single-walled nanotube with 278 symmetry operations.
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Preface

The text of this thesis is based on the research conducted at Rice University. The most important findings and results have been published in the following paper:

- Alexander A. Rusakov, Michael J. Frisch, and Gustavo E. Scuseria. Space group symmetry applied to SCF calculations with periodic boundary conditions and Gaussian orbitals.

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Chapter 1

Introduction

Effective one-electron approximations are of prime importance for the electronic structure modeling of extended systems, including formally infinite objects such as structures periodic in 1, 2, or 3 dimensions (crystals). Among these approximations, density functional theory (DFT) undoubtedly remains one of the most powerful, popular, and even one of the very few affordable tools to perform calculations on large systems, often making those routine tasks [1]. Theoretical foundations of DFT were laid by Hohenberg and Kohn [2], while Kohn and Sham proposed the most widely-used formulation of the theory by introducing an idealized system of non-interacting electrons in an external potential to yield the same ground-state density as a real system would [3]. The entire difference between an idealized system and a real one is embraced by the (unknown) exchange-correlation functional (XCF). The development of the theory along the lines of the Kohn–Sham formulation consists essentially in building various approximations of XCFs based on a large span of arguments from the first-principle derived analytic properties [4] of the functionals to empirical fits, for instance [5,6].

Several detailed hierarchies of the XFC approximations have been proposed by Staroverov and Scuseria in [7,8]. For the present discussion, the classification known as the “Jacob’s ladder” (alluding to Gen. 28:12) proposed by Perdew [9] appears more convenient. This ladder is deemed to connect the world of the Hartree–Fock approximation with the world of attaining chemical accuracy and has five steps, or
rungs, which are local spin-density functional, generalized gradient approximation, meta-generalized gradient approximation (*i.e.* including high order derivatives of density), functionals depending on occupied orbitals, and functionals depending on vacant orbitals.

Though models of the “pure” functionals of the first three rungs are widely used, their failures are not uncommon [10]. Significant quantitative failures have been observed, for instance, in modeling even simple organic reactions [11] and predicting lattice constants of molecular crystals [12]. One of the egregious examples of qualitatively wrong behavior of simple XFC models is prediction of metallic properties of UO$_2$ known to be an insulator [13].

The forth rung of the ladder contains an especially important class of functionals with orbital dependence via one-particle density matrix known as hybrid functionals. The idea of admixing a fraction of exact, or Hartree–Fock-type exchange (HFx, the use of the former term in this context has been disputed in [7]), was initially proposed by Becke [14] and was supported by further theoretical findings by Perdew, Ernzerhof, and Burke [15]. To prove a definitive successes of hybrid functionals, it would suffice to mention the extremely widely used functional B3LYP [14, 16]. Remarkably, incorporating HFx has been found to provide remedy to the cases of qualitative failure of semi-local models, as in the highlighted case of UO$_2$ [13]. Noteworthy, admixing HFx to pure functionals leads to only a moderate increase of computational cost for molecular systems, thus contributing to the popularity of such scheme.

Application of simply designed global hybrid functionals (such as B3LYP, B3PW91, PBE0) to extended systems and primarily crystals is noticeably more limited, while a number of reports have been published. Among properties studied are band gaps [13, 17–20], lattice constants [13, 19, 20], bulk moduli [19, 20], spin magnetic mo-
ments [19]. Though the hybrid schemes employed resulted in superior performance over the pure ones, the applicability of global hybrids appears limited due to both theoretical and performance issues. The former arises from combining exact exchange and approximate correlation, leading to qualitatively wrong behavior at large distances between electrons [21]. Computationally, unlike molecules or even 1D periodic systems, relative increase of a calculation cost is very pronounced for 3D crystalline species [21], especially in narrow-gap materials with one-particle density matrices slowly decaying with the increase of the distance between electrons.

With the advent of a new generation of hybrid functionals, different from simple mixing schemes, a substantially more efficient treatment of HFx 3D solids became possible. Devising range-separated, or screened, functionals [22, 23] provides partial treatment for both theoretical and computational issues typical for global hybrids when applied to extended systems.

Splitting the Coulomb potential into short- and long-range components and retaining the former only enables significant reduction of the number of two-electron integrals to be computed for HFx, though without a noticeable loss of accuracy [24,25]. The Heyd–Scuseria–Ernzerhof (HSE) functional based on the global PBE-hybrid contains only one empirically adjusted parameter determining separation between short- and long-range. This approximation has been assessed for various solids. Not has is only enjoyed outstanding success in predicting band gaps, bulk moduli, and lattice constants [24,26–32], but allowed to address crystal defects [33].

Efficiency of DFT with hybrid functionals in extended systems is strongly dependent on the scaling properties of the method. Techniques based on the fast multipole method (FMM) [34, 35] or Ewald potential function [36] facilitate linear scaling of the Coulomb problem, at least in the far-field region. Linear scaling of the exchange-
correlation part of the Kohn–Sham procedure can be also attained [37].

Efficient FMM-based approaches are not directly applicable to the HF\textsubscript{x} problem due to a different from Coulomb algebraic structure of contracting two-electron integrals with density matrices, though other sophisticated screening techniques enable linear scaling of this part as well [38]. Nevertheless, even with linear scaling made feasible, the computation cost associated with a still large number of explicitly evaluated two-electron integrals can easily get demanding for systems with large unit cells, e.g., structures with defects or chiral nanotubes.

The bottleneck of the SCF procedure for periodic systems consists in explicit evaluation of a large number of two-electron integrals required for both HF\textsubscript{x} part (typically the most expensive) and the near-field Coulomb problem. Since crystalline structures often have rather high symmetry described by space groups (in 3D-periodic systems; for 1D- and 2D-periodic systems line and layer groups are used), the entire pool of two-electron integrals gets split into classes of equivalent ones. Thus the need to calculate only one integral representing the set results in substantial reduction of the total number of handled integrals and leads to noticeable savings in computational time of the most expensive steps.

Though symmetry-based reduction of the number of two-electron integrals has been addressed as early as in 1970’s and has become routine, the extension of this technique to periodic structures received much less attention. Space-group symmetry has been explored in the CRystal group [39–41] and is available in the program. This achievement, however, is restricted to the use of symmorphic groups, which amounts to point groups upon imposing periodic boundary conditions (PBC), and a very special case of non-symmorphic groups for achiral nanotubes. We therefore aspire to developing a method capable of dealing with any space (and, in general,
layer and line) group, both symmorphic and non-symmorphic.

Throughout this work, we will be referring to the electronic (non-relativistic) Hamiltonian expressed in the basis of Cartesian Gaussian type orbitals. This discretization (some comparison with the plane-wave method is given, for example, in [42] and references therein) is advantageous primarily due to the ease of analytically evaluating molecular integrals. The localized form of Gaussian basis functions also plays a key role in screening procedures and attaining linear scaling [38, 43–47].
Chapter 2

Theoretical background

2.1 Reduction of the two-electron integrals list for molecules

The idea of making SCF calculations cheaper by taking advantage of spatial symmetry in reducing the number of explicitly evaluated molecular, especially two-electron integrals of the general form (Mulliken notation used here)

\[(ij|kl) = \int \phi_i^*(1)\phi_j(1)\frac{1}{r_{12}}\phi_k^*(2)\phi_l(2)d1d2, \quad (2.1)\]

had been initially proposed in [48], though derived for the Coulomb contribution only.

This approach has been developed in much more detail in [49], though still laid out for the Coulomb term, and discussed later in [50] for the general case of two-electron contributions. The exhaustive theoretical account of applying point-group symmetry to reject equivalent two-electron integrals has given by Dupuis and King in [51]. Their derivation stems from symmetric properties of the molecular Fock matrix and the use of the reduced (“petite”) lists of the quartets of basis functions entering the expression of the two-electron integral (Eq. 2.1).

It has been shown [51] that the Fock-type matrix has the symmetry of the molecule, i.e.

\[F = R^\dagger FR, \quad (2.2)\]

where \(R\) is a symmetry operation of the molecular point group and \(R\) is the corresponding transformation of the basis set \(\phi_i, i = 1, n\). Identical, i.e. pertaining
to the atoms of the same type and having identical radial and angular parts, basis functions sharing symmetrically equivalent centers are considered equivalent, i.e. if \( r_1 = (R|t) \), then \( r \sim r_1 \), \( \phi_i(r) \sim \phi_i(r_1) \) (here \( r \) stays for the Gaussian orbital center, not for the electron coordinate). Fig. 2.1 illustrates this using an example of a benzene molecule and basis functions centered on carbon atoms (we do not display hydrogen atoms just for the sake of the image clarity). Identical basis functions \( \phi_i(r) \) and \( \phi_i(r_1) \) appear equivalent under a counterclockwise rotation by \( \pi/3 \) around the 6-fold axis passing through the molecule center perpendicular to the image.

Likewise, pairs of centers mapping onto one another as a whole under symmetry operations lead to equivalent pairs of basis functions \( [\phi_i(r_1)\phi_j(r_2)] \sim [\phi_i(T_1)\phi_j(T_2)] \), as shown in Fig. 2.2.

Finally, mapping of the quartets of centers results in the equivalence of the quartets of basis functions: \( [\phi_i(r_1)\phi_j(r_2)\phi_k(r_3)\phi_l(r_4)] \sim [\phi_i(T_1)\phi_j(T_2)\phi_k(T_3)\phi_l(T_4)] \) if \( r_m \sim T_m, m = 1,4 \), see also Fig. 2.3. The entire set of two-electron integrals is thus split into equivalence classes, with chosen single representatives thereof forming the reduced, or “petite” list.

If the two-electron contribution is calculated based on the “petite” list of integrals it is referred to as skeleton \( G_{sk} \). The fundamental result of Ref. [51], crucial for the discussion to follow, is that the full two-electron contribution \( G \) to the Fock matrix \( F \) can be fully restored by symmetrization of the skeleton two-electron matrix \( G_{sk} \).

The symmetrization step consists in computing the following sum of the images of \( G_{sk} \) where \( i \) runs over all operations of the molecular point group:

\[
G = \sum_{i=1}^{n} R_i^t G_{sk} R_i. \tag{2.3}
\]

Noteworthy, symmetrization (Eq. 2.3) can be performed on both Coulomb and exchange contributions independently, therefore this technique is applicable not only to
Figure 2.1: Equivalent basis functions

Figure 2.2: Equivalent pairs of basis functions; functions forming a pair are connected with dashed lines
the Hartree–Fock matrix, but also to the Fock-type one in Kohn–Sham DFT.

2.2 Space-group symmetry

We treat crystalline systems as formally infinite and strictly periodic in 1, 2, or 3 dimensions. Our focus is mostly on systems periodic on all 3 directions (3D), unless mentioned otherwise. Periodicity imposes existence of an infinite countable sets of points $\mathbf{r}$ sometimes referred to as a crystal pattern [52] or equivalently as a lattice and vectors $\mathbf{t}$ known as lattice vectors:

$$\mathbf{t} = a_1 \mathbf{t}_1 + a_2 \mathbf{t}_2 + a_3 \mathbf{t}_3,$$

with $\mathbf{t}_i$ being (primitive) lattice vectors. Crystal pattern (lattice) and lattice vectors form an affine space with $\mathbf{t}$ acting on any $\mathbf{r}$ to yield another crystal pattern point. In this regard one can view operations ($\mathbf{I}|\mathbf{t}$), where $\mathbf{I}$ is an identity operation in 3D, acting on points $\mathbf{r}_1 = \mathbf{I}\mathbf{r} + \mathbf{t} = \mathbf{r} + \mathbf{t}$ as affine transformations. These operations obviously form a group, which is a translation subgroup $\mathbf{T}$ of 3D isometries, or the 3D Euclidean group.

Apart from translational symmetry, a lattice is always invariant with respect to inversion due to a simple fact that for any lattice vector $\mathbf{t}$, $-\mathbf{t}$ is also a lattice vector. Periodicity in 2 or 3 dimensions imposes constraints on rotational symmetry of lattice, enabling rotation and inversion axes of the orders 2, 3, 4, and 6 only. Therefore, only 32 point groups, known as crystallographic groups, are pertinent to accounting for a 2- or 3-dimensional lattice. No such restriction applies to the 1D case [53, 54].

The symmetry of an actual nD structure, i.e., a spatial arrangement of real atoms which obeys strict periodicity in 1, 2, or 3 dimensions is described by line, layer, or space groups, respectively [53, 54]. There is an infinite number of line groups (these
contain a subclass of 75 rod groups which are subgroups of space groups), 80 layer groups, and 230 space groups. An arbitrary operation of a space group $G$ can be represented as $(R|t)$ where $R$ is a $3 \times 3$ orthogonal transformation matrix and $t$ is a shift which, unlike in Eq. 2.4, is not necessarily a pure lattice vector from $T$. An arbitrary point is then transformed as

$$r_1 = (R|t)r = Rr + t \quad (2.5)$$

Space groups can be split into two classes: symmorphic and non-symmorphic groups. Qualitatively, this separation can be based on whether the group operations can be decomposed to lattice translations and point-group orthogonal transformations, or it includes transformations that cannot be separated into consecutive rotation (reflection) and translation. In the latter case operations such as screw axes and glide plains appear, in which only a combination of rotation or reflection followed by translation by a fraction of the lattice vector is a symmetry mapping — not when those components are taken apart — see, e.g., Fig 2.4 displaying symmetry operations of the non-symmorphic group $P6_3/mmc$. For the goal we pursue in this work, this qualitative argument would not suffice, and a more rigorous consideration appears helpful.

For a given space group, the set of rotation (reflection, inversion) matrices $R$’s is finite and has as many elements as the corresponding crystallographic point group. We can establish a mapping, which is readily proven to be a homomorphism,

$$H : (R_i|\tau + T) \rightarrow (R_i|0), \quad (2.6)$$

where $(R_i|\tau + T)$ stays for the infinite set of operations sharing the same $R_i$, $\tau$ is a shift other than a full lattice translation, $0 \leq \tau_i < 1$. 
Figure 2.3: Equivalent quartets of basis functions: the original quartet is given in black, the image — in red.

Figure 2.4: NiAs: example of the non-symmorphic group $P6_3/mmc$. 
For any lattice translation, \( H((I|t)) = (I|0) \), therefore the translational subgroup \( T = \ker(H) \) is the homomorphism kernel. Moreover, since any \( T \) element obviously commutes with any element of \( G \), \( T \) is a normal subgroup. Therefore, decompositions of \( G \) into left and right cosets with respect to \( T \) coincide, and the cosets \((R_i|\tau) (I|T)\) form a factor-group:

\[
G/T = \{(R_i|\tau) (I|T)\}.
\]  

(2.7)

This setup brings us exactly within the conditions of the so-called homomorphism theorem that claims isomorphism between a homomorphous image of a group and a factor-group with the respect to the homomorphism kernel. Thus,

\[
\{(R_i|\tau) (I|T)\} \sim \{(R_i|0)\} = \{R_i\}
\]

(2.8)

where \( \{R_i, i = 1, \ldots, n\} \) is the crystallographic point group.

It is worth noting that the image \( \{R_i, i = 1, \ldots, n\} \) is not bound to be a subgroup of \( G \), nor does it have even to be a subset of \( G \), still being a group. If \( \{R_i, i = 1, \ldots, n\} \) is a subgroup of the space group, the entire space group can be represented as a semi-direct product of \( \{R_i, i = 1, \ldots, n\} \) and \( T \),

\[
G = T \rtimes \{R_i, i = 1, \ldots, n\},
\]

(2.9)

and is called symmorphic. There are totally 73 symmorphic space groups. The remaining 157 groups do not contain their crystallographic point group as a subgroup and are called non-symmorphic. These groups, in addition to regular translations, rotations, reflections, and inversion, acquire symmetry operations known as screw axes and glide plains with rotations and reflections followed by a shift by a fraction of the primitive lattice vector.

The \((R_i|\tau)\) operation originating a coset is called a coset representative. It is worth noting that for a symmorphic group, one can choose a \((R_i|0)\) representative
for any coset with these representatives forming a group. For non-symmorphic groups, representatives will have a non-trivial translational part $\tau$ and thus will not form a group: their multiplication will amount to a full lattice translation, which is not in the set. This notion will be important in the following discussion regarding the reduction of the list of two-electron integrals based on the operations of non-symmorphic, as well as symmorphic groups. Since translational symmetry — as it follows from the discussion right below — is essentially exploited in the formulation of the SCF theory for periodic systems, separation of pure translations becomes the matter of both theoretical and practical considerations.

### 2.3 SCF equations with PBC

In strictly periodic systems, effective one-electron operators $\mathbf{F}$, such as the Fock or the Kohn–Sham operator, comply with the conditions of the Bloch theorem [55], therefore the set of SCF equations can be decoupled in reciprocal, or $k$-space, with each $k$-point associated with an irreducible representation of the group of pure translations $\mathbf{T}$:

$$\mathbf{F}^k \mathbf{C}^k = \mathbf{S}^k \mathbf{C}^k \epsilon^k. \quad (2.10)$$

This decoupling is achieved in the basis of Bloch functions, each of those, for a given $k$, being a basis of one-dimensional (since $\mathbf{T}$ is Abelian) irreducible representation of $\mathbf{T}$. If one departs from discretizing the (direct-space) Fock-type, i.e. Fock or Kohn–Sham, operator in the set of localized functions (such as Gaussian-type functions) centered on atomic nuclei, the Bloch sums are formed:

$$\psi^k = N \sum_g \phi_g \exp(i \mathbf{k} \cdot \mathbf{g}), \quad (2.11)$$

where $N$ stays for normalization, $\mathbf{g}$ runs over the crystal cells and specifies the location
of identical localized functions $\phi$. In the entire discussion, Gaussian-type orbitals $\phi$ are used, as introduced by Boys [56]:

$$\psi(x, y, z) = x^l y^m z^n \exp(-\alpha r_A^2), \quad (2.12)$$

where $x_A = x - A_x$ (same for $y$ and $z$), $r_A^2 = x_A^2 + y_A^2 + z_A^2$, $\alpha > 0$ is the exponential parameter.

The Fock-type matrix element between the Bloch sums $\psi^k_M$ and $\psi^k_N$, stemming respectively from localized functions $\phi_\mu$ and $\phi_\nu$, can be easily shown to result from a Fourier transformation of the direct space Fock-type matrix of a special kind [34]:

$$F^k_{MN} = \sum_g F^{0g}_{\mu\nu} \exp(i \mathbf{k} \cdot \mathbf{g}). \quad (2.13)$$

The format of the direct-space matrix $F^{0g}_{\mu\nu}$ indicated that one localized basis function always resides on the central, or reference, 0-cell, with $g$ allowed to be in an arbitrary cell, including 0. In practical calculations, the range of $g$ is limited to a finite portion of crystal. Thus, imposing translational symmetry and, therefore, equivalence of unit cells, reduces the completely intractable problem to the one embracing only interactions of one picked cell with rest of the crystal, as shown in Fig. 2.5.

As in the molecular case, $F^{0g}_{\mu\nu}$ splits into the kinetic energy, nuclear attraction (external potential), Coulomb repulsion, and exchange (in Hartree–Fock) or exchange-correlation (in DFT) terms. Exact, or Hartree–Fock-type exchange (HFx) appears in density-matrix dependent (hybrid) functionals and is algebraically analogous to the one in the Hartree–Fock case. Though a significant part of the Coulomb term can be efficiently incorporated using various techniques based on classical treatment of the charge distributions [34], if those obey certain conditions of being well separated (far-field contributions), the near-field Coulomb (J) and HFx (K) contributions have
to be computed explicitly via contracting two-electron integrals with one-electron density matrices:

\[ J_{\mu\nu}^0 = \frac{1}{2} \sum_{m,n,\lambda,\sigma} (\mu_0 \lambda_m | (\lambda_0 \sigma_n)_m) P_{\lambda\sigma}^{0n} \]  

(2.14)

\[ K_{\mu\nu}^0 = \sum_{m,n,\lambda,\sigma} (\mu_0 \lambda_m | (\nu_0 \sigma_n)_g) P_{\lambda\sigma}^{0,n-m} \]  

(2.15)

In extended systems, evaluation of the terms (2.14) and (2.15) is typically the bottleneck of the calculation. Reduction of the list of two-electron integrals based on the system symmetry is therefore crucial in facilitating computations on such systems.

### 2.4 Extension of the Dupuis and King technique to the periodic case

The derivation of the method in Ref. [51] does not necessarily require the pairs \[ [\phi_i(r_1) \phi_j(r_2)] \] forming the quartets to be taken from the same set. Inspection of the expressions for the Coulomb Eq. 2.14 and exchange Eq. 2.15 contributions reveals that the only difference of the right-hand side of the two-electron integrals (here presented in Mulliken notation) from the molecular case consists in the shift of the whole pair of basis functions by a lattice vector (translational invariance of the density matrix was tacitly assumed in Eqs. (2.14, 2.15)). Fig. 2.4 shows the pairs contributing to the general \( (\mu_0 \nu_g | (\lambda_0 \sigma_n)_m) \) two-electron integral.

Since the crystal is formally infinite, all shifts are permissible, and the right-hand sides form a closed set under the symmetry operations mapping the crystal onto itself, therefore validating the applicability of the basic statements of Ref. [51] to \( F_{\mu\nu}^0 \).

In other words, the way the direct space Fock matrix is specified for the PBC case can be viewed as essentially molecular, since a finite portion of a crystal is taken for a practical calculation. The only difference consists in neglecting interactions between
Figure 2.5: $\mathbf{F}^{\text{lag}}_{\mu\nu}$ interaction of the rest of the crystal

Figure 2.6: Shifted pair in a general two-electron integral
cells both being other than the central one. This observation makes the molecular
approach theoretically transferrable to periodic structures, but gives rise to a number
of implementation issues to be discussed below.

Choosing the list of the unique quartets for the periodic case according to the
technique proposed in Ref. [51] and further developed in Refs. [39,40] requires several
subtleties to be considered. These subtleties result from

- the way the crystalline structure is specified for a calculation;
- the direct space Fock-type matrix format;
- the use of non-symmorphic groups.

2.4.1 Crystalline structure specification

The structure is determined as an atomic pattern within a reference cell translated
throughout the entire space via lattice vectors. For instance, the full structure of dia-
mond (space group $Fd\bar{3}m$) is unambiguously specified by two atoms and a set of three
rhombohedral translations. Obviously, there is an infinite number of combinations of
atomic patterns and translation vectors that would result in the same structure. This
specification, however, imposes attribution of given atoms to a certain cell, as one
can clearly infer from Fig. 2.7. In Fig. 2.7, the central cell of a square lattice is shown
in bold. Two atoms: one at the origin (0; 0) and the other one in the center of the
square (1/2; 1/2) — together with translation vectors provide a complete description
of the structure. Thus, only atoms (0; 0) and (1/2; 1/2) belong to the central cell,
while atoms (0; 1), (1; 0), and (1; 1), though geometrically falling into the central cell,
belong to different cells, specified by translation vectors (0; 1), (1; 0), and (1; 1), re-
spectively. As it can be seen from Fig. 2.8, a different choice of a unit cell — $OA''A'B$
Figure 2.7: Attribution of atoms to unit cells

instead of $OAA'B$ — leads to a different set of atoms considered as belonging to the central cell.

Generally, only atoms with fractional coordinates $(x, y, z)$ such that $g_1 \leq x < g_1 + 1, g_2 \leq y < g_2 + 1, g_3 \leq z < g_3 + 1$ belong to the cell originating at $g = (g_1, g_2, g_3)$. It is worth noting that application of a four-fold axis passing through the center of the square perpendicular to the plain of Fig. 2.7 to the atom at $(0; 0)$ would thus move this atom outside the unit cell, though the interior part of the cell remains invariant. This observation is in close relation with maintaining the proper format of the Fock-type matrix under symmetry transformations.

2.4.2 The direct space Fock-type matrix format

First, as it was mentioned above, the direct-space Fock-type matrix format is such that one basis function must always reside in the reference cell. Second, lower-triangular storage is normally assumed, i.e. $\mu \geq \nu$ in $F_{\mu\nu}^0$. In general, these require-
ments may not be satisfied automatically upon forming symmetry images of $F_{\mu \nu}^0$'s. If the first condition is not fulfilled, and the image $\overline{\mu}$ appears in some cell $h \neq 0$, then, due to translation invariance of integrals and densities, the pair can be translated by the lattice vector $-g$. For the second condition the right mapping is achieved by noting that $F_{\mu \nu}^0 = F_{\nu \mu}^0 - g$. We address this in detail in the Method and implementation section.

2.4.3 Applying non-symmorphic groups

Translational symmetry has been already used by imposing periodic boundary conditions (PBC) and the corresponding format of the Fock-type matrix, as described in Section 2.3. The remaining operations to consider should, at least qualitatively, be the space group operations devoid of pure lattice translations. These operations emerge naturally for symmorphic groups: since the representatives of the cosets of the quotient group $G/T$ can be chosen in the form $(R|0)$. Such representatives form a group (which is simply the crystallographic point group) and can be applied straightforwardly.
The translational component \( \tau \) cannot be eliminated simultaneously in all coset representatives if \( G \) is non-symmorphic, as discussed in Section 2.2. Regardless of the choice, the resulting set of representatives does not form a group, since forming the products of such representatives eventually amounts to generating a full lattice translations not present in the set.

It has been noticed [57] that when applied to functions with translational symmetry, these representatives act like a group. Since the entities of our main interest — direct space Fock-type matrices and two-electron integrals — are translationally invariant, \((R|\tau)'\)'s in their matrix representation can be formally used along with \((R|0)\) operations: if a full lattice translation emerges, the above mentioned equivalence is taken advantage of. This can be viewed as redefining the group operation (“multiplication”) by reducing the products of the matrices ’modulo 1’, i.e., retaining only the components of the translation part (in fractional coordinates) \(0 \leq \tau_i < 1\).

Fig. 2.9 illustrates how the requirements imposed on two-electron integrals and Fock-type matrices formats affect applying regular and screw axes to atoms for the case of the layer (with 2D lattice) group \( p2_1 22 \) (no. 20 in Ref. [54]). Applying \((R|t)\) representatives, we follow the nucleus that carries the basis function to be retained in the central cell. A 2-fold rotation brings the nucleus \( A \) to \( 2(A) \), \( 2_1 \) axis — to \( 2_1(A) \). Upon applying either regular 2 or screw \( 2_1 \) axis both functions appear outside the central cell. To satisfy the condition imposed, those two images should be translated back to the unit cell to become respectively \( 2(A)' \) and \( 2_1(A)' \). It is worth noting that regardless of the operation type — regular or screw rotation — the necessity to translate a basis function back, along the lines of the DeAngelis argument [57], eliminates the essential differences in applying operations of symmorphic and non-symmorphic groups.
Figure 2.9: Applying operations of 2 and $2_1$ axes in $p2_122$ group. Based on symmetry elements image from International Tables for Crystallography (2006). Vol. E, Layer group 20, pp. 262–263.
Due to practical reasons, it is convenient to use symmetry operations in the form they are represented in the International Tables for Crystallography, vol. A [53]. According to Sections 2.11. and 11.1.1. [53], the coordinate triplets of the general position (reduced ‘modulo 1’) represent the symmetry operations of the space group in the matrix form. Let us notice that for centered lattices the number of symmetry operations considered is $N + 1$ times larger ($N$ is the number of centering vectors) than the order of the factor-group thus yielding the complete general position explicitly.
Chapter 3

Method and implementation

In this chapter we discuss in detail schemes for reducing the number of two-electron integrals by rejecting symmetry-equivalent shell quartets, building the skeleton Fock-type matrix and its symmetrization to restore the full one. This approach aims at exploiting the full space group symmetry based on theoretical foundation discussed in the previous chapter.

3.1 Preliminary comments on reducing shell quartets

Following the discussion in the previous chapter, we can introduce equivalent basis functions and their pairs for periodic systems, as shown in Figs. 3.1 and 3.2 for a simplistic case of a square lattice with a 4-fold axis perpendicular to the image.

The equivalence \( \phi_i(r) \sim \phi_i(r_1) \sim \phi_i(r_2) \sim \phi_i(r_3) \) under \( \pi/2 \) rotations includes individual functions belonging to different unit cells. Analogously, equivalence is established between the pairs of basis functions: for instance, \([\phi_i(r_0)\phi_j(r_1)] \sim [\phi_i(r_0)\phi_j(r_2)]\), \([\phi_i(r_0)\phi_k(r_3)] \sim [\phi_i(r_0)\phi_k(r_4)]\) (we did not display other pairs equivalent under the 4-fold axis to keep the plot clear).

A straightforward approach would consist in applying the whole set of symmetry operations to each individual quartet of basis functions (or shells) and retaining only one representative of the resulting set. A simplistic example of a quartet transformation under a 4-fold rotation is given in Fig. 3.3 with the quartet
\[ \phi_i(r_0)\phi_j(r_1)\phi_k(r_2)\phi_l(r_3) \] being equivalent to \[ \phi_i(r_0)\phi_j(r_1')\phi_k(r_2')\phi_l(r_3') \]. Likewise in Fig. 3.2, we display only two quartets for the sake of the plot clarity.

Certain priority can be assigned to each quartet. For instance, one can calculate some unique index based on the indices of basis functions and the cells they appear in. Then, transforming each quartet upon applying symmetry operations, one can save it if the priority of its images is lower than of the original one, and dismiss it otherwise. This is essentially the way the quartet selection is performed for molecules, since the number of quartets is rather moderate, and so is the number of symmetry operations, yielding a very rough estimate for the number of operations needed for selection being \( N^4 \cdot N_{op} \), where \( N \) is the number of basis functions, \( N_{op} \) is the group order.

The same estimate of the integral selection cost for a periodic system would be roughly \( N^4 \cdot N_{cel}^3 \cdot N_{op} \), where \( N \) is the number of basis functions per unit cell and \( N_{cel} \) is the number of cells used for a particular calculations. Since \( N_{cel} \) can be of the order of \( 10^3 \), and \( N_{op} \) can be up to 192 for cubic space groups, selecting the unique quartets and assembling the information for a batch of two-electron integrals can be as expensive as the very evaluation thereof, thus making the straightforward approach inefficient and calling for a different technique to employ.

There are two possibilities to form the reduced list of shell quartets without direct quartet selection. Such list would naturally emerge if symmetry-unique unshifted pairs, which are the left-hand sides of the two-electron integral expression, are coupled with all possible shifted pairs, or the right-hand sides. Alternatively, right-hand sides can be reduced by symmetry and coupled with all possible, \( i.e., \) not subject to any selection left-hand sides. Both approaches are introduced in detail in the discussion to follow.
3.2 Reduction based on unique left-hand side shell pairs

The left-hand side pairs always retain one function in the 0-cell under symmetry transformations. If this requirement is not satisfied (see Fig. 3.4), by applying shifts, it is restored. Since such pairs, whether shifted or not, are coupled with all possible right-hand sides, the existence of a universal list of reduced left-hand sides is assured, assuming the crystal is formally infinite. This is, in general, not the case for the reduced right-hand sides, as we will discuss later.

It might be noticed that in practical calculation, the infinite crystal is restricted to a finite system which, in general, is not bound to comply with the symmetry of the full crystal. The immediate effect is that not every pair (or quartet) within such finite portion has its symmetry-related counterpart. Therefore, if a given pair upon at least one operation generates an image which is not present in the system, then this system should be either extended to include all images, or it should be dismissed with all the images. In general, this can affect the resulting energy. Nevertheless, these special pairs occur with one basis function being at the very periphery of the finite crystal sample and has a negligible contribution to the answer, thus keeping this problem purely formal.

Let \( I^0 \) represent the index of the shell \( I \) in the central cell, \( J^g \) — the index of the shell \( J \) in an arbitrary cell \( g \), \( N \) is the total number of shells within single unit cell. Then the algorithm of rejecting symmetry equivalent unshifted shell pairs can be organized as follows.

Algorithm 1

1. Ascribe a unique index to every \((I^0, J^g)\)-pair, e.g.

\[
\text{Index} = I(I - 1)/2 + J + gN(N + 1)/2
\]  \hspace{1cm} (3.1)
2. For every \((I^0J^g)\)-pair, loop over all symmetry operations and form symmetry images \((I^hJ^{g'})\). One should notice that \(I'\) acquires a cell index \(h\) as the nucleus carrying the shell may not necessarily stay within the reference cell upon applying a symmetry operation, as shown in Fig. 3.4.

If \(h \neq 0\), then both shells \(I'\) and \(J'\) are shifted by a cell vector \(-\mathbf{h}\) corresponding to the cell with index \(h\) thus yielding \((I^0J^{g''})\), \(g'' = g' - h\). Let us note that this situation occurs even for operations of symmorphic groups, for instance, a simple 4-fold axis (in centered as well as primitive lattices), as illustrated. At the same time, the imposed format restriction reflecting translational invariance allows one to use operations of the non-symmorphic groups the same way as in the symmorphic ones.

If \(I' < J'\), the equivalent pair is \((J^0I^{g''})\), \(g''' = -g''\).

3. Calculate the Index' of the shifted pair using Eq. (3.1). If Index' > Index, remove the \((I^0J^g)\) pair from the list and continue with the next pair, otherwise keep it. If \(M\) operations of the space group map the retained pair onto itself, \(\text{Index}' = \text{Index}\), ascribe it the weight factor \(1/M\).

The algorithm above is always applied to the near-field Coulomb problem to provide compatibility with the FMM code used to address the far-field one.

Though being universal and reasonably straightforward to implement, Algorithm 1 may not be able to provide the highest attainable gain in speed. Fig. 3.5 is aimed at illustrating the origin of this shortcoming. We consider a simple cubic structure (space group \(Pm\bar{3}m\)) with atoms of two types \((z = 0\) and \(z = 1/2\), those being different atoms; one can consider, for instance, the CsCl structure which can be viewed as two interpenetrating primitive lattices of Cs and Cl atoms). Only the layer of the central
cell (in bold) is shown for clarity.

Atomic positions in the reference cell may have high local symmetries, i.e. their site-symmetry groups (Section 3.4. in Ref. [58]) are non-trivial, and there is at least one symmetry operation, rather than identity, that leaves the given point invariant. (Since pure translations have been already withdrawn from consideration, site-symmetries of positions are different from what one could see in the crystallographic tables as Wyckoff positions. In our example we are dealing with simply the point group $m\overline{3}m$, and not with the space group $Pm\overline{3}m$.) Thus, for instance, the function $I^0$ residing on a atom in $m\overline{3}m$ position remains intact under all 48 operations of the group. Therefore, none of the two-electron integrals containing the $(I^0 I^0)$-pair can be rejected, though there are obviously equivalent quartets to yield such integrals. The $J^0$ function centered on the nucleus of $3m$ position (that is, it remains invariant under all operations of the point group $3m$) can produce 8 distinct images, thus allowing to reduce the number of integrals containing the $I^0 J^0$-pair by the factor of 8 only.

Another restriction comes from applying shifts. Since, for example, the $J^0$ functions either maps onto itself (6 times due to $3m$ site symmetry) or appears outside the 0-cell, the $J^0 J^0$-pair, similarly to the $I^0 I^0$ one, maps 48 times onto itself, enabling no reduction for integrals stemming from such pair.

One can notice however, that the same functions centered outside the unit cells, e.g., $I^g$ and $J^{g_1}$, have lower site symmetries, $mm2$ and $m$ respectively, thus being able to generate 12 and 24 images. If the multiplicity of such position is low: a small number of distinct points is generated upon applying group operations — the unshifted pairs list reduction can be noticeably restricted. This observation prompts considering the alternative approach, i.e., performing symmetry-based rejection of the shifted, or right-hand sides followed by coupling the surviving pairs with all possible
left-hand sides.

### 3.3 Reduction based on unique right-hand side shell pairs

Lower site-symmetry of functions outside the central cell suggests that more substantial reduction of the number of two-electron integrals can be attained by applying symmetry to the right-hand sides instead of the left-hand sides. Let us consider integrals resulting from \((I^0 I^0 | J^0 J^0)\) (see Fig. 3.5), totally 24 integrals. According to the discussion above, applying symmetry to the left-hand side would result in no reduction, while for the right-hand side presumable reduction would be by the factor 24. Similar arguments can be put forward for other combinations of basis functions.

As it turns out, forming the list of the reduced right-hand sides is way less straightforward than for the left-hand sides. The main problem here is, however, that the universal list of reduced shifted pairs does not necessarily exist. Fig. 3.6 illustrates the problem for the case of an abstract square lattice with atoms in the corners and in the center of the cell.

To avoid overloading in Fig. 3.6, we consider only the pairs of basis functions sharing the same nuclei. We also restrict the set of symmetry operations to a 4-fold rotational axis passing through the origin perpendicular to the figure plain. The shell pair \((I^0_1 J^0_0)\) at the origin remains intact under all 4-fold rotations due to its site symmetry 4 (or 4/mmm, if all actual operations are considered). The images of the pair \((I^0_2 J^0_2)\) appear out of the central cell under 4-fold axis operations and are required to be brought back to the central cell, therefore the shell pair \((I^0_2 J^0_2)\) also stays intact upon a \(\pi/2\) counterclockwise rotation. The pair \((K^q_1 L^q_1)\) results from translating the \((K^q_1 L^q_0)\), and \((K^{q^p}_1 L^{q^p}_1)\) denotes the symmetry images of \((K^q_1 L^q_1)\) upon the counterclockwise \(\pi/2\) rotation. As it can be seen, the pairs \((K^q_1 L^q_0)\) and \((K^{q^p}_1 L^{q^p}_1)\)
remain symmetrically equivalent with respect to the central cell pair \((I_1^0, J_1^0)\), but they do not do so with respect to the pair \((I_2^0, J_2^0)\) which is subject to a shift.

This observation remains valid for any situation if there is at least one symmetry operation that brings at least one atom of the central cell outside its boundaries and thus induces a translation back to it.

Forming the universal list of shifted pairs remains possible if there is a subset \(G'\) (still applied in the ‘modulo 1’ sense, as before) of operations which leave all nuclei of the reference cell within this cell. Such set, in general, is not bound to contain point group operations only, but can still include screw axes and glide plains as well. If a non-trivial set \(G'\) exists, the following Algorithm 2 enables further reduction of the two-electron integrals list.

**Algorithm 2**

1. Perform reduction of the unshifted (rooted in the 0-cell) pairs following Algorithm 1

2. Form the initial list of the right-hand sides by applying all lattice translations to the reduced list of the left-hand sides. Due to all possible (within, practically, a selected portion of a crystal) translations being applied, the resulting right-hand side list is universal, though possibly redundant.

3. Loop over the index of the retained pairs. If the pair is retained with the weigh factor 1, *i.e.*, it never maps unto itself for any non-trivial operation, further reduction is impossible, and the pair should be left intact for all shifts.

4. If a pair is retained with a fractional weight, then loop over all shifts.

5. Apply symmetry operations of \(G'\) to the shifted pair. If the pair itself, not
including the cell translation, is changed by the symmetry operation, proceed to the next operation: the image has been already rejected. As the cell index also changes once the operations are applied, consider only one of them (for instance, the largest) for the shifted pair to be left, and reject all other pairs generated by $G'$. Since shifted pairs can also be mapped onto themselves by certain symmetry operations, the resulting weight factor should be adjusted accordingly.

### 3.4 Note on implementation

The reduced lists of shell pairs are processed by the PRISM [59] algorithm for calculating the two-electron integrals and the Fock matrix formation, as implemented in *Gaussian* [60] program. An obviously desired feature of all schemes for symmetry-based reduction of the list of two-electron integrals is that the amount of CPU time required is negligible compared to integral evaluation itself. So must perform the internal PRISM schemes for assembling batches of two-electron integrals.

Due to a relatively small number of left-hand sides, or unshifted pairs $(I^0J^0|$, rejection based on a straightforward loop over such pairs is computationally inexpensive. In forming the batches of integrals, the unshifted pairs are in the outer loop. If a pair weight factor is 0, *i.e.*, the pair is dismissed, then the entire set of two-electron integrals stemming from it is not processed at all. Therefore, neither the loop over right-hand sides, nor, if needed, screening procedures of the corresponding integrals are performed, leading to substantial savings before the very calculation of the surviving integrals is done.

The situation is noticeably different if the rejection is based on the right-hand sides $|(K^0L^0)^h)$. The number of these pairs is roughly $N_{cel}$ times larger than that of
$(I^0 J^g)$ pairs. Moreover, the $|(K^0 L^g)^h)$ loop appears within the $(I^0 J^g)$ one, and the weights (1 if a pair is retained, 0 if rejected, $1/M$ if mapping onto itself $M$ times) of $|(K^0 L^g)^h)$'s are different for each $h$. This combination leaves no space for rejecting integrals across the board, as with the left-hand side style selection. As a result, the full double $(I^0 J^g|(K^0 L^g)^h)$ loop is as expensive as in a non-symmetric case. It turns out from test calculations that it can readily take longer than the evaluation of the surviving integrals itself. Moreover, additional work has to be done by the screening procedure to eliminate the integrals with 0 weights coming from the symmetry-based selection.

To avoid this somewhat unexpected and disappointing drawback of the $|(K^0 L^g)^h)$-based selection, we have introduced several algorithmic modifications. The list of $|(K^0 L^g)^h)$'s is cleared of all pairs with zero weight before the quartets are formed. Since to form a batch of integrals of a certain length (to enable optimal performance of the subsequent integral computation) the first and the last $KL$-indices are provided by the code, those are mapped onto $(KL)'$-indices of the reduced array. Thus, if $(KL)'_{\text{begin}} > (KL)'_{\text{end}}$, such integrals are automatically skipped, and a batch is being formed using different $(KL)'_{\text{begin}}$ and $(KL)'_{\text{end}}$. By implementing this modified way of accessing the $|(K^0 L^g)^h)$-pairs we immediately avoid forming quartets with zero weight due to symmetry selection and thus eliminate all work needed to remove them from already formed batches.

The schemes proposed above have been implemented in the Gaussian [60] development version. While the left-hand side rejection is always used for the near-field Coulomb part, the decision for HFx is made based on whether there is a non-trivial $G'$ set.
3.5 On the possibility of getting beyond left- or right-hand side rejection

As follows from the discussion above, direct selection of the basis functions quartets appears highly inefficient for periodic systems. At the same time, the proposed schemes for left- or right-hand sides rejection, though computationally feasible, may not necessarily lead to the largest possible reduction of the two-electron integral list. Individual selection of quartets can be still considered as an option upon preliminary reduction of the list of two-electron integrals based on the technique already developed.

A provisional approach would require forming not only the list of weights for the \( (I^0 J^g) \) pairs, but also the array of symmetry images of the pairs under symmetry operations together with shifts incurred to bring the pair back to its format, if both functions appear outside the unit cell. The following reduction of preliminary selected integrals thus requires:

- applying a symmetry operation to a surviving quartet

\[
\mathbf{R}[(I^0 J^g | (K^0 L^{g_1} )^h)] = (I'^{g'} J'^{g''} | (K'^0 L'^{g_2} )^{h'}) ; \tag{3.2}
\]

- translating the entire transformed quartet by \(-g'\):

\[
(I'^{g'} J'^{g''} | (K'^0 L'^{g_2} )^{h'}) \rightarrow (I'^{g'''} J'^{g''''} | (K'^0 L'^{g_2} )^{h''}), \tag{3.3}
\]

where \( g''' = g'' - g' \), \( h''' = h' - g' \);

- retaining only one representative of the set resulting from Eq. 3.3;

- adjusting the surviving quartet the weight factor \(1/M\), \(M\) counting the number of mapping the quartet onto itself.
Possible benefit of this method, as distinct from the straightforward selection, comes from applying selection to the list of quartets which has been already substantially reduced by left- or right-hand side selection. Nonetheless, applying all symmetry operations to each surviving quartet, the smallest possible number whereof is \( N_{\text{initial}}/N_{op} \), makes the overall benefit not so obvious. This scheme has not been implemented yet. The work is in progress and will be reported in due time.

3.6 Obtaining the full Fock-type matrices

Restoration of the full Fock matrix from the skeleton one \( i.e., \) resulting from the reduced list of integrals, can be in principle performed straightforwardly according to Eq. (2.3). Keeping in mind the format of the Fock-type matrix, \( F^0_{I,J} \), the symmetrization process can be naively organized as a 4-fold loop:

- over \( N_{op} \) symmetry operations;
- over \( N_{cel} \) cells;
- over \( N \) \( I \)-basis functions residing in the \( 0 \)-cell;
- over \( 1,\ldots,I \) \( J \)-basis function residing in any cell (lower diagonal storage of \( F \) is assumed).

The innermost loop, therefore, contains applying a rotation matrix to the chosen segment of the Fock matrix and adding the resulting image to a new appropriate location. As it has been already noticed in describing Algorithm 1, an arbitrary symmetry operation transforms the pair \( (I^0,J^g) \) to the pair \( (I^h,J^{g'}) \), therefore the symmetry image of \( F^0_{I,J} \) is \( F^{h,g'}_{I,J} \) where \( h \) can be different from \( 0 \). Due to transla-
tional invariance of the Fock matrix $\mathbf{F}_{ij} = \mathbf{F}_{h_i h_j}^{g_i g_j}$, and the relation $\mathbf{F}_{ij}^{0g} = \mathbf{F}_{j_i}^{0,-g}$ the symmetry contribution from $\mathbf{F}_{ij}^{0g}$ is $\mathbf{F}_{i'_j}^{0,-h} g$, if $I' \geq J'$, or $\mathbf{F}_{j'_i}^{0,-h} g'$, if $I' < J'$.

A naive 4-fold loop can be computationally inefficient if rather extended basis sets are used, since it would require to find the image location (the cell image) for each pair of functions. It is therefore much more convenient to calculate the cell image for each pair of atoms instead, thus slightly transforming the inner part of the loop:

- loop over $N_{at}$ in cell $0$;
- loop over $1, \ldots, I_{at}$ in cell $g$;
  
  determine the image of $g$ for a given pair of atoms;
- loop over basis functions centered on the atom of the given pair.

Finally, though the Fock matrix is stored in the lower-diagonal form, certain algorithmic convenience comes from bringing the skeleton matrix to square form before symmetrization and restoring it back to the original format afterwards. The symmetrization scheme of the PBC Fock-type matrix has been also implemented in the Gaussian [60] development version. If HFx exchange evaluation is performed in the case of hybrid functionals, symmetrization is done at the very end of the cycle when both Coulomb and HFx parts are consolidated into one two-electron contribution.
Figure 3.1: Symmetry-equivalent basis functions in square lattice under 4-fold rotation
Figure 3.2: Symmetry-equivalent pairs of functions in square lattice under 4-fold rotation
Figure 3.3: Symmetry-equivalent quartets in square lattice under 4-fold rotations
Figure 3.4: Equivalence of shell pairs. \((I^hJ^g)\) results from a \(\pi/2\) rotation of \((I^0J^g)\), but should be shifted by as a whole by \(-h\) to yield \((I^0J^{g''})\).
Figure 3.5: Local symmetries of atomic positions in an abstract $Pm\bar{3}m$ structure with two types of atoms. The layer of the central cell is shown.
Figure 3.6: On existence of a universal reduced list of right-hand side pairs. Pairs $(K_1^g L_1^g)$ and $(K_1^{g'} L_1^{g'})$ are equivalent w.r.t. $(I_1^0 J_1^0)$, but not w.r.t. $(I_2^0 J_2^0)$. 
Chapter 4

Benchmark calculations and computational efficiency

4.1 General remarks on 3D-periodic systems

We have tested our new code against the conventional Gaussian [60] program for the following systems: C (diamond), Si (diamond-like structure), ZnS (zincblend and wurtzite), GaN (wurtzite-type structure), BaS, and BN. The screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) [61] is employed in all our calculations. All structural parameters, basis sets, and effective core potentials are taken from Ref. [32], where the assessment of the HSE functional for various crystalline structures was reported.

For these tests, we have chosen the smallest possible unit cells: two atoms per cell for C, Si, zincblend, and BaS, four atoms for wurtzite-type structures and BN. In most cases, these cells are not conventional crystallographic unit cells as described in Table 2.1.2.1. in Ref. [53], and the set of primitive translational vectors at the origin is not left invariant under the operations of the point group of the lattice. Nevertheless, all operations of the space groups are used since they still comply with the structure. This choice brings in the restrictions we need to apply using Algorithms 1 and 2, thus deliberately forcing the code work in a presumably unfavorable environment. The results are summarized in Table 4.1. We report speedup factors for the PRISM algorithm at the most expensive steps of evaluating the near-field Coulomb matrix
and HFx as observed during a single iteration of the SCF cycle.

4.2 Diamond-like structures

Diamond and silicon structures (Fig. 4.1) have $Fd\bar{3}m$ symmetry with 192 symmetry operations (group no. 227 in [53]). Since we are setting the smallest rhombohedral unit cell with primitive translations being halves of face diagonals of the conventional cell — see Fig. 4.1, we are effectively using 48 operations ((0, 0, 0) set, as listed in [53]). Two atoms within the unit cell are equivalent (under inversion and a glide plain).

Speedup factors for diamond are 9.2X for the near-field Coulomb problem, 6.0X and 8.2X for HFx (left- and right-hand side selection, respectively), but for silicon they are only 4.2X (Coulomb), 5.3X and 5.6X (HFx). This may appear surprising, since both species have similar structure. Possible explanation of such unusual behavior can be drawn from the notion that in diamond, lattice constant is $ca. 1.5$ times smaller than in silicon. In the near-field Coulomb problem, the distance-based criterion of shell pairs being well-separated is imposed. Thus, in the diamond structure a larger fraction of two-electron integrals appears in the near field and has to be treated explicitly than in silicon. The fractional coordinates (not the Cartesian ones!) of the centers contributing to the explicitly evaluated integrals reach larger (absolute) values and appear in less symmetric positions facilitating a more pronounced reduction of the integrals due to symmetry in diamond.

A similar effect is observed in the HFx problem, though due to a different reason: in the screened HSE functional [61], a system-independent parameter to split the $1/r_{12}$ operator into short- and long-range parts is introduced. Since only the short-range exchange is retained, the span of the fractional coordinates of the contributing atomic centers is wider in diamond than in silicon, resulting in a larger fraction of
integrals rejected based on symmetry equivalence.

According to this explanation, one could expect more dramatic speedup in HFx if a global hybrid such as PBE0 was used. Unfortunately, to the best of our knowledge, in the absence of screening such calculation gets absolutely impracticable.

4.3 Rock salt type: barium sulfide

Rock salt type structures (Fig. 4.2) are of $Fm\overline{3}m$ symmetry with 192 operations (group no. 225 in [53]). This group is symmorphic and results from a semi-direct product of $m\overline{3}m$ point group and a face-centered lattice. As in the previous example, primitive rhombohedral cell is used, Fig. 4.2. Speedup factors appear noticeably smaller than in the previous example: 2.0X (Coulomb), 2.4X and 3.4X (HFx). In addition to the lattice constant argument (BaS has even larger lattice constant than Si), one should notice that atoms within the unit cell are obviously not equivalent and occupy highly symmetric positions.

4.4 Zinc sulfides: zincblend and wurtzite

Zincblend structure (Fig. 4.3) is of cubic $F\overline{4}3m$ symmetry, described by a symmorphic group (no. 216 in [53]), while the other crystalline structure of ZnS — wurtzite (Fig. 4.4) — is hexagonal described by a non-symmorphic group $P6_3mc$ (no. 186 in [53]). One can notice that though the former has 96 operations and the latter — only 12, the speedup factors: 3.7X vs. 3.0X for Coulomb and 2.8X vs. 2.6X for HFx, — are comparable prompting that non-symmorphic groups provide more flexibility for our methods of integral selection.
Figure 4.1: Diamond and silicon: conventional and primitive unit cells

Figure 4.2: BaS: conventional and primitive unit cells
4.5 Nitrides: BN and GaN

These hexagonal boron (Fig. 4.5) and gallium (Fig. 4.6) nitrides are described by non-symmorphic space groups $P6_3mc$ (see above) and $P6_3/mmc$ (no. 194, 24 operations [53]), respectively. We can notice again that non-symmorphic groups, even with a relatively small number of operations, provide speedups comparable with those in symmorphic groups with a large number of operations.

All reported results on 3D systems are summarized in Table 4.1.

Let us notice that even though the systems chosen for the tests possess high symmetry, the atoms occupy special positions, i.e., are mapped onto themselves by non-trivial operations. Due to the low multiplicity of such special positions, the resulting speedup factors are noticeably lower than the number of operations used. This observation is in agreement with the earlier findings in Ref. [41]

4.6 On importance of operations of non-symmorphic groups in 3D

As we have already mentioned, previously reported approaches are based on the use of symmorphic groups only, i.e., exploiting point-group symmetry upon making use of translational invariance. Since we extend the method to incorporate any space group, it is worth testing whether adding screw axes and glide plains results in any substantial increase of speedup factors.

We have performed a simple test to evaluate the importance of non-symmorphic group operations in the resulting speedup factors. Using the same settings for diamond as above and the STO-3G basis set, we reduce the symmetry from $Fd\bar{3}m$ (group No. 227, 192 operations) to $F\bar{4}3m$ (group No. 216, 96 operations). In the lat-
Table 4.1: Speedup factors (SF) are given for the near-field Coulomb (NF J, left-hand side reduction) and HFx (left-hand side reduction (L) and right-hand side reduction (R), if available).

<table>
<thead>
<tr>
<th>System</th>
<th>Space group, number of operations</th>
<th>SF, NF J</th>
<th>SF, HFx</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Fd3m, 192</td>
<td>9.2</td>
<td>6.0</td>
</tr>
<tr>
<td>Si</td>
<td>Fd3m, 192</td>
<td>4.2</td>
<td>5.3</td>
</tr>
<tr>
<td>BaS</td>
<td>Fm3m, 192</td>
<td>2.0</td>
<td>2.4</td>
</tr>
<tr>
<td>ZnS (zincblend)</td>
<td>F43m, 96</td>
<td>3.7</td>
<td>2.8</td>
</tr>
<tr>
<td>ZnS (wurtzite)</td>
<td>P63mc, 12</td>
<td>3.0</td>
<td>2.6</td>
</tr>
<tr>
<td>GaN</td>
<td>P63mc, 12</td>
<td>3.3</td>
<td>2.8</td>
</tr>
<tr>
<td>BN</td>
<td>P63/mmc, 24</td>
<td>4.3</td>
<td>3.9</td>
</tr>
</tbody>
</table>
Figure 4.4: ZnS — wurtzite: crystalline structure and primitive unit cells
ter calculation, evaluation of the HFx contribution with the right-hand side reduction is slower by the factor of 1.5 compared to the former.

4.7 Quasi-1D systems: achiral and chiral single-walled carbon nanotubes

If atomic positions are of high multiplicity, the system is expected to display more significant reduction of the computational time. Single-walled carbon nanotubes appear one of the convenient objects to observe speedup factors comparable to the number of the symmetry operations used.

It is worth noting that there is a certain discord in literature regarding the symmetry properties of nanotubes, including the single-walled ones. Thus, for example, in Refs. [62, 63] achiral tubes, *i.e.* having inversion or mirror plains as symmetry operations, are claimed to be described by symmorphic groups, as opposed to chiral tubes. In [64] it is claimed that any single-walled nanotube is described by some non-symmorphic group, since achiral tubes always have a special kind of screw axis: for instance, \((n, 0)\) and \((n, n)\) single-walled nanotubes (SWNT) have \(2n/n\) screw axes \((\pi/n \text{ rotation followed by translation by } 1/2 \text{ of the primitive translation})\). We are inclined to consider the latter approach as a more comprehensive one.

Symmetry has been successfully exploited in studies of the electronic properties of various quasi-1D systems, such as chrysotile [65], carbon [66], imogolite [67], and magnesium oxide [68] single-walled nanotubes. All studied species are achiral \((n, −n)\) for chrysotile, \((n, 0)\) and \((m, m)\) otherwise) tubes. In all works [65–68], the authors claim that the full rototranslational symmetry is employed. At the same time, the authors of [65–68] always refer to point symmetry when discussing the direct-space
Fock-type matrix evaluation, making it not so clear, which set of operations is being used.

We applied our technique to both achiral (Figs. 4.7 and 4.8) and chiral (Figs. 4.9 and 4.10) SWNT’s. The geometries were generated using the Tubegen [69] program. We used only point groups to describe the symmetry of achiral SWNT’s. The symmetry properties of the chiral tubes (7,4) (Fig. 4.9) and (16,7) (Fig. 4.10) are taken from [70].

These two latter tubes are characterized by a general type of screw axis $C_{m/n}$: the group generating operation consists of a rotation by $\phi = 2\pi n/m$ and a shift by $1/m$ of the primitive translation vector. For the (7,4) tube we use the same basis set as for diamond, while for numerical experiment with the (16,7) tube we restrict ourselves to the minimal STO-3G set.

In Table 4.2, we report our findings in several test runs of the program. Speedup factors are given, as above, for the PRISM algorithm computing the near-field Coulomb and HFx parts per one SCF iteration. Results in Table 4.2 show that substantial speed up factors between 9–70X for the near-field Coulomb and 9–57X for HFx can be achieved for these carbon nanotubes.
Figure 4.5 : BN: crystalline structure and primitive unit cells

Table 4.2 : Speedup factors (SF) for single-walled carbon nanotubes. Near-field Coulomb (NF J) and HFx. Left-hand side reduction only.

<table>
<thead>
<tr>
<th>System</th>
<th>Symmetry group, number of operations</th>
<th>SF, NF J</th>
<th>SF, HFx</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6,0)</td>
<td>$D_{6h}$, 24</td>
<td>9.3</td>
<td>8.9</td>
</tr>
<tr>
<td>(15,0)</td>
<td>$D_{15h}$, 60</td>
<td>22.0</td>
<td>21.3</td>
</tr>
<tr>
<td>(7,4)</td>
<td>$C_{62/17}$, 62</td>
<td>28.0</td>
<td>29.0</td>
</tr>
<tr>
<td>(16,7)</td>
<td>$C_{278/121}$, 278</td>
<td>69.7</td>
<td>56.7</td>
</tr>
</tbody>
</table>
Figure 4.6: GaN: crystalline structure and primitive unit cells
Figure 4.7 : (6,0) SWNT

Figure 4.8 : (15,0) SWNT
Figure 4.9: (7,4) SWNT
Figure 4.10: (16,7) SWNT
Chapter 5

Conclusions

In this work we explored application of space group symmetry to SCF calculations, primarily Kohn–Sham DFT, with periodic boundary conditions and Gaussian orbitals. As distinct from previously reported approaches, our method facilitates any non-symmorphic space, layer, and line groups. Efficient algorithms for selecting symmetry-unique two-electron integrals have been developed and implemented in the development versions of Gaussian code. Benchmark calculations on the simple solids with smallest unit cells display substantial speedup factors in evaluating near-field Coulomb and Hartree–Fock-type exchange contributions. We show that inclusion of the operations of non-symmorphic groups results in a noticeable gain in speed even in a simple system setup. Applied to quasi-1D systems with low site-symmetry of the atomic positions, our methods lead to speedup factors for the same contributions to exceed one order of magnitude, potentially allowing studies of chiral objects with helical symmetry and large unit cells.
Bibliography


