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REGULAR ARTICLE

A practical scheme for ab initio determination of a crystal structure based on the Dirac equation

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Abstract An applicable formulation of ab initio crystal structure determination based on the Dirac equation is presented. For this purpose, Dirac equation without regard to electron correlation effects is reduced to its spin-free one-component form by means of regular approximations, and then, connected to crystallographic notions. Thus, a relativistically valid structural description of a crystal structure is made possible by using single crystal X-ray diffraction data. The relativistic scheme was tested with a previously reported crystal structure containing heavy elements, and the results show that accuracy of the phase assignment process increases as the order of regular approximation is raised.

Keywords Dirac equation · Regular approximations · X-ray crystallography · Phase problem

1 Introduction

The number of crystal structures of the compounds containing heavy elements deposited in Cambridge Structural Data Base (CSD), in which relativistic effects become more visible than light organic compounds, has exponentially increased in recent years [1]. The relativistic corrections on the crystal structure determination for the compounds containing heavy elements were examined by many authors [2–4]. They endeavored to incorporate the relativistic effects into crystallography by calculating the atomic scattering factors for various elements via Dirac–Hartree–Fock wave functions without modifying conventional formulation of X-ray crystallography. X-rays are collectively scattered by both the innermost and outermost electrons of an atom, and the X-ray diffraction experiments on crystalline materials give us only a set of measured intensities of diffracted beams. If the amplitudes and the phases of diffracted X-ray beams can be found, electronic density distribution, or in other words, positions of atoms in the unit cell can be obtained by a Fourier transform. The recovery of the phases from only the magnitudes of diffracted X-ray beams is termed the "*phase problem*" and it is of a great importance in development of conventional crystal structure determination procedure. In this regard, our primary interest will be addressed to improvement of alternative methods in order to obtain a relativistically valid systematic procedure of crystal structure determination for such compounds without solving conventional phase problem by incorporating with experimental data.

The importance of relativistic effects [5] in chemistry of the compounds containing heavy elements has been already well recognized. For relativistically treating the effects arising from the existence of heavy elements, one has to solve the Dirac equation instead of the Schrödinger equation. The Dirac equation involves a four-component Hamiltonian and generates negative energy eigenstates besides positive ones. The solutions with negative energy indicating the existence of positronic states are generally neglected by chemists because of the fact that chemical properties of a system are essentially related to its electronic states. Therefore, the four-component Dirac equation is reduced to two parts called as the *large* (for electronic states) and *small* component (for positronic states). If this can be done without a significant loss of accuracy in the calculations, the *exact* large component is fully equivalent to the four-component electronic solutions. In order to separate electronic and positronic solutions, there are several different methods such as Foldy-Wouthuysen (FW) transformation [6], Douglas–Kroll (DK) [7], Douglas–Kroll–Heß(DKH) [8,9] and relativistic scheme

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by eliminating small component (RESC) [10]. Among these methods, DK (or DKH) approximation, which supplies an efficient way of handling the matrix elements of two-component Hamiltonian, has tractable results in the presence of non-singular operators corresponding to electron–nucleus attraction. Although RESC method is based on density functional formalism [11–13], FW transformation has also serious singularity problems [14]. An alternative scheme known as regular approximation (RA) [15–18] has been proposed to avoid the presence of singular operators especially observed in vicinity of the nucleus. The regular Hamiltonian methods have been competitive to the DKH approach with some of the latest improvements in RA[19–22]. However, the spin information of electrons has been implicitly included in the Dirac equation or other two-component Hamiltonians. Treatment of these equations in spin-dependent form is of mathematical difficulties. Since RAs are mathematically more convenient than the other two-component methods in order to attain our purpose here, they can be used to take into consideration the relativistic features in the theory of crystallography.

To determine a crystal structure and to enhance structural information from a routine X-ray crystallographic study, several alternative methods having regard to only quantum mechanical principles have been developed in recent years [23–25]. Among them, Bethanis et al. [24] showed that the ab initio determination of the positions of the nuclei in a crystal can be achieved by exploiting the time-independent Schrödinger equation for an electron without regard to electron–electron repulsive interactions. Although such an oversimplification seems to be inappropriate for a satisfactory quantum mechanical description for the system of interest, Bethanis et al. have showed that it suffices to obtain acceptable results about the positions of nuclei. Here, crystallographic notions are incorporated into Schrödinger-like spin-free one component form of the Dirac equation by working within the momentum space. In this regard, molecular wave functions in momentum space have to be considered inevitably. It has been previously reported that the repulsive electron–electron interactions in a molecule do not change the total momentum but in turn lead to an inter-electronic momentum transfer between each pair of electrons [26]. As a result of this, the phase invariance in one-electron Schrödinger-like equation also holds for the exact equation including inter-electronic repulsive interactions. Here, the term of “*phase invariance*" means that the phase of the Fourier transform of an eigenfunction is invariant under the potential multiplication (or convolution operation in momentum space) [24].

2 Theory

In this section, an overview of regular approximations required for derivation of pertinent relativistic equations is presented in a succinct manner. Let us consider the four-component Dirac equation for an electron under the effect of an external potential V:

$$\hat{H}_D \Xi_D = E \Xi_D, \tag{1}$$

where (in atomic units; $\hbar = 1$, $m_e = 1$, $4\pi\varepsilon_0 = 1$, $c = 137.03599$)

$$\hat{H}_D = c\boldsymbol{\alpha}\hat{\mathbf{p}} + \boldsymbol{\beta}c^2 + (V - c^2)\mathbf{1}, \tag{2}$$

or in two-component matrix form

$$\hat{H}_D = \begin{pmatrix} V & c\boldsymbol{\sigma}\hat{\mathbf{p}} \\ c\boldsymbol{\sigma}\hat{\mathbf{p}} & V - 2c^2 \end{pmatrix}, \tag{3}$$

and the 4-spinor for wave function Ξ_D is defined as

$$\Xi_D = \begin{pmatrix} \chi^L \\ \chi^S \end{pmatrix}. \tag{4}$$

Here, L and S denote the large and small component of the 4-spinor, respectively. In addition, the standard symbols are used for Dirac ($\boldsymbol{\alpha}$, $\boldsymbol{\beta}$) and Pauli spin ($\boldsymbol{\sigma}$) matrices and $\mathbf{1}$ is the 4×4 unit matrix. Other symbols have their usual meanings.

Using the exact FW (EFW) transformation [27] defined as

$$\hat{U} = \begin{pmatrix} \frac{1}{\sqrt{1+\hat{X}^\dagger\hat{X}}} & \frac{\hat{X}^\dagger}{\sqrt{1+\hat{X}^\dagger\hat{X}}} \\ \frac{-\hat{X}}{\sqrt{1+\hat{X}\hat{X}^\dagger}} & \frac{1}{\sqrt{1+\hat{X}\hat{X}^\dagger}} \end{pmatrix}, \tag{5}$$

the part of Hamiltonian for the positive energy states resulting from the unitary ($\hat{U}^\dagger = \hat{U}^{-1}$) EFW transformation ($\hat{H}_{\mathrm{EFW}} = \hat{U}\hat{H}_D\hat{U}^{-1}$) is

$$\begin{aligned} \hat{h}^+_{\mathrm{EFW}} = & \frac{1}{\sqrt{1+\hat{X}^\dagger\hat{X}}} \\ & \times \left(V + c\boldsymbol{\sigma}\hat{\mathbf{p}}\hat{X} + \hat{X}^\dagger c\boldsymbol{\sigma}\hat{\mathbf{p}} + \hat{X}^\dagger(V - 2c^2)\hat{X}\right) \\ & \times \frac{1}{\sqrt{1+\hat{X}^\dagger\hat{X}}}, \end{aligned} \tag{6}$$

and the transformed 4-spinor is

$$\Xi_{\mathrm{EFW}} = \begin{pmatrix} \frac{\chi^L + \hat{X}^\dagger\chi^S}{\sqrt{1+\hat{X}^\dagger\hat{X}}} \\ \frac{-\hat{X}\chi^L + \chi^S}{\sqrt{1+\hat{X}\hat{X}^\dagger}} \end{pmatrix}. \tag{7}$$

From the off-diagonal elements of the $\hat{H}_{\mathrm{EFW}}$ matrix, it follows that $\hat{X}$ must satisfy [27]

$$2c^2\hat{X} + [\hat{X}, V] + \hat{X}c\boldsymbol{\sigma}\hat{\mathbf{p}}\hat{X} = c\boldsymbol{\sigma}\hat{\mathbf{p}}, \tag{8}$$

so that the lower 2×1 part of the transformed 4-spinor is vanished. In other words, the last equation means that operator $\hat{X}$ has the special property to connect the large and small components of the Dirac 4-spinor,

$$\chi^S = \hat{X}\chi^L. \tag{9}$$

Using Eq. (9) into Eq. (7), for the solutions with positive energy, one can easily obtain

$$\Xi^{+}_{\mathrm{EFW}} = \sqrt{1+\hat{X}^{\dagger}\hat{X}}\,\chi^{L}. \tag{10}$$

The exact $\hat{X}$ can be obtained for a given eigenstate of the Dirac equation as

$$\hat{X} = \frac{c}{2c^2 - V + E}\boldsymbol{\sigma}\hat{\mathbf{p}}, \tag{11}$$

if it operates on the large component of the eigenstate with eigenvalue E. In order to avoid the energy dependence in Eq. (11), an expansion can be used as follows

$$\begin{aligned}\frac{1}{2c^2 - V + E} &= \frac{1}{2c^2 - V}\left(1 + \frac{E}{2c^2 - V}\right)^{-1} \\ &= \sum_{n=0}^{\infty} \frac{(-1)^n E^n}{(2c^2 - V)^{n+1}}.\end{aligned} \tag{12}$$

The term in the bracket above is of importance to make such an expansion. The expansion is valid for $|E| < 2c^2$, which implies the case for all bound states. For large V, close to the nucleus, this approximation is written in terms of inverse powers of the potential. For small V, this expansion is stated by powers of c^{-2} far from the nucleus. Since the energy-dependent terms in the expansion is small for relatively small E, it is reasonable to neglect them. In the light of this approximation, $\hat{X}$ in Eq. (11) is reduced to its following definition

$$\hat{X} = \frac{c}{2c^2 - V}\boldsymbol{\sigma}\hat{\mathbf{p}}. \tag{13}$$

Inserting this definition of $\hat{X}$ into the $\hat{h}^{+}_{\mathrm{EFW}}$ Hamiltonian, one can obtain the regular FW-Hamiltonian $\hat{h}_{\mathrm{RFW}}$ defined as

$$\hat{h}_{\mathrm{RFW}} = \frac{1}{\sqrt{1+\hat{X}^{\dagger}\hat{X}}}\left(V + \boldsymbol{\sigma}\hat{\mathbf{p}}\frac{c^2}{2c^2 - V}\boldsymbol{\sigma}\hat{\mathbf{p}}\right)\frac{1}{\sqrt{1+\hat{X}^{\dagger}\hat{X}}}. \tag{14}$$

The term within the bracket in Eq. (14) is the well-known ZORA (zeroth order regular approximation) Hamiltonian

$$\hat{h}_{\mathrm{ZORA}} = V + \boldsymbol{\sigma}\hat{\mathbf{p}}\frac{c^2}{2c^2 - V}\boldsymbol{\sigma}\hat{\mathbf{p}}. \tag{15}$$

The ZORA Hamiltonian may be written as follows

$$\hat{h}_{\mathrm{ZORA}} = V + \frac{1}{2}\boldsymbol{\sigma}\hat{\mathbf{p}}\hat{\mathcal{R}}\boldsymbol{\sigma}\hat{\mathbf{p}}, \tag{16}$$

where

$$\hat{\mathcal{R}} = \frac{1}{1 - \frac{1}{2}\alpha^2 V} = 1 + \frac{1}{2}\alpha^2\hat{\mathcal{R}}V, \tag{17}$$

and α is the fine structure constant defined as $\alpha = 1/c$. The ZORA Hamiltonian in powers of α^2 is

$$\hat{h}_{\mathrm{ZORA}} \approx \frac{1}{2}\hat{p}^2 + V + \frac{1}{4}\alpha^2\boldsymbol{\sigma}\hat{\mathbf{p}}V\boldsymbol{\sigma}\hat{\mathbf{p}}. \tag{18}$$

An improvement over ZORA is obtained by the first-order terms with respect to the metric perturbation [11,14,28] and brings about what is called as the FORA (first order regular approximation) Hamiltonian:

$$\begin{aligned}\hat{h}_{\mathrm{FORA}} \approx{}& V + \frac{1}{2}\boldsymbol{\sigma}\hat{\mathbf{p}}\hat{\mathcal{R}}\boldsymbol{\sigma}\hat{\mathbf{p}} - \frac{1}{8}\alpha^2(\boldsymbol{\sigma}\hat{\mathbf{p}}\hat{\mathcal{R}}^2\boldsymbol{\sigma}\hat{\mathbf{p}}V + V\boldsymbol{\sigma}\hat{\mathbf{p}}\hat{\mathcal{R}}^2\boldsymbol{\sigma}\hat{\mathbf{p}}) \\ & - \frac{1}{16}\alpha^2(\boldsymbol{\sigma}\mathbf{p}\hat{\mathcal{R}}^2\boldsymbol{\sigma}\hat{\mathbf{p}}\boldsymbol{\sigma}\hat{\mathbf{p}}\hat{\mathcal{R}}\boldsymbol{\sigma}\hat{\mathbf{p}} + \boldsymbol{\sigma}\hat{\mathbf{p}}\hat{\mathcal{R}}\boldsymbol{\sigma}\hat{\mathbf{p}}\boldsymbol{\sigma}\hat{\mathbf{p}}\hat{\mathcal{R}}^2\boldsymbol{\sigma}\hat{\mathbf{p}}),\end{aligned} \tag{19}$$

whose α-expansion recovers all terms of well-known Pauli Hamiltonian:

$$\begin{aligned}\hat{h}_{\mathrm{FORA}} ={}& \frac{1}{2}\hat{p}^2 + V + \frac{1}{4}\alpha^2\boldsymbol{\sigma}\hat{\mathbf{p}}V\boldsymbol{\sigma}\hat{\mathbf{p}} - \frac{1}{8}\alpha^2(\hat{p}^2V + V\hat{p}^2) \\ & - \frac{1}{8}\alpha^2\hat{p}^4 + \cdots\end{aligned}$$

3 Relativistic X-ray crystallography

The Hamiltonians given in Eqs. (18) and (19) are still in spin-dependent form. To obtain spin-independent one-component Hamiltonians, let us first consider the Hamiltonian given in Eq. (16). If the operator $\hat{\mathcal{R}}$ in Eq. (17) is expanded in terms of the powers of potential, and then this expansion is inserted in Eq. (16), one can obtain a spin-free one-component form as follows,

$$\hat{h}_{\mathrm{ZORA}} \approx \frac{\hat{p}^2}{2} + V - \frac{1}{8}\alpha^2\hat{p}^4 + \frac{1}{32}\alpha^4\hat{p}^6. \tag{20}$$

Similarly, FORA Hamiltonian in Eq. (19) can be also written as

$$\hat{h}_{\mathrm{FORA}} \approx \frac{\hat{p}^2}{2} + V - \frac{1}{8}\alpha^2\hat{p}^4 + \frac{1}{16}\alpha^4\hat{p}^6. \tag{21}$$

While obtaining the last two equations, the fact that one can approximately set $\frac{1}{2}\alpha^2\hat{p}^2 \approx -\alpha^2 V$ in the regions close to the nucleus is used to avoid infinitely large potential terms. This setting is reasonable because large values of V are reduced because of simultaneously large values of p^2. This approximation arises from the Virial theorem and it is also valid for the regions far from the nucleus. In this way, we avoid from the presence of the terms $\hat{p}^2V$ and $V\hat{p}^2$ in the Pauli Hamiltonian or extra convolution summations in the relativistic scheme as we will encounter in the next stage for derivation of the required equations.

The inclusion of crystallographic notions into the relativistic quantum chemistry can be achieved by mapping the problem into the Fourier space. The question is whether the electron density map is possible to obtain from the relativistic quantum mechanics with the unknown phases of the crystal structure factors. To see that it is possible, let us start with the ZORA eigenvalue equation. ZORA eigenvalue–eigenfunction equation in position space is

$$\left(\frac{\hat{p}^2}{2} + V(\mathbf{r}) - \frac{1}{8}\alpha^2\hat{p}^4 + \frac{1}{32}\alpha^4\hat{p}^6\right)\psi(\mathbf{r}) = \epsilon_{\mathrm{ZORA}}\psi(\mathbf{r}), \tag{22}$$

and its counterpart in Fourier (or momentum) space is defined as

$$\frac{p^2}{2}\varphi(\mathbf{p}) - \frac{1}{8}\alpha^2 p^4\varphi(\mathbf{p}) + \frac{1}{32}\alpha^4 p^6\varphi(\mathbf{p}) + W(\mathbf{p}) \otimes \varphi(\mathbf{p}) = \epsilon_{\mathrm{ZORA}}\varphi(\mathbf{p}), \tag{23}$$

where $W(\mathbf{p})$ and $\varphi(\mathbf{p})$ are the Fourier transformation of $V(\mathbf{r})$ and $\psi(\mathbf{r})$, $\otimes$ stands for the convolution operation, ϵ_{ZORA} is the ZORA energy eigenvalue regardless of repulsive electron–electron interactions. At this point, keeping in mind that the phase of the Fourier transform of an eigenfunction is invariant under the potential multiplication operation (or convolution operation in momentum space), further theoretical developments may be achieved by the connection between the momentum space and the diffraction theory. Unless otherwise stated after here, bold capital letters indicate the reciprocal lattice vectors. Thus, for $\mathbf{p} = 2\pi\mathbf{H}$ we have:

$$\varphi(\mathbf{p}) = \varphi(2\pi\mathbf{H}) = (2\pi)^{-3/2}\Phi(\mathbf{H}), \tag{24}$$

$$W(\mathbf{p}) = W(2\pi\mathbf{H}) = (2\pi)^{-3/2}\tilde{W}(\mathbf{H}). \tag{25}$$

Furthermore, the Fourier coefficients $W(\mathbf{p}) = W(2\pi\mathbf{H})$ of the potential function $V(\mathbf{r})$ can be stated in terms of the normalized structure factors $E(\mathbf{H})$ well-known in crystallography defined as

$$E(\mathbf{H}) = \sum_{j}^{N}\frac{Z_j\exp(2\pi i\mathbf{H}\cdot\mathbf{r}_j)}{\gamma}, \tag{26}$$

where

$$\gamma = \sqrt{\sum_{j}^{N} Z_j^2},$$

N is the number of atoms in the unit cell and Z_j is the atomic number of the jth atom [1, Chap. 6, p. 436]. The relation between the Fourier coefficients $W(\mathbf{p})$ of the potential function and the normalized structure factors $E(\mathbf{H})$ is as follows [24];

$$W(\mathbf{p}) = -(2\pi)^{-3/2}\frac{\gamma}{\pi H^2}E(\mathbf{H}). \tag{27}$$

A noteworthy fact is that the potential term in momentum space has a unique singularity at the origin of momentum space, whereas the potential term in coordinate space has N singularities each of which is located at the position of nucleus. Since the convolution integral in Eq. (23) can be replaced by a discrete sum for a crystal, Eq. (23) can be rewritten as follows

$$\Phi(\mathbf{H}) = \frac{(\gamma/\pi)}{\left(2\pi^2\mathbf{H}^2 - 2\alpha^2\pi^4\mathbf{H}^4 + 2\alpha^4\pi^6\mathbf{H}^6 - \epsilon_{\mathrm{ZORA}}\right)} \times \sum_{\mathbf{K}\neq\mathbf{H}}\frac{E(\mathbf{H}-\mathbf{K})\Phi(\mathbf{K})}{|\mathbf{H}-\mathbf{K}|^2}. \tag{28}$$

Similarly, another equation which is valid under the first order regular approximation is that

$$\Phi(\mathbf{H}) = \frac{(\gamma/\pi)}{\left(2\pi^2\mathbf{H}^2 - 2\alpha^2\pi^4\mathbf{H}^4 + 4\alpha^4\pi^6\mathbf{H}^6 - \epsilon_{\mathrm{FORA}}\right)} \times \sum_{\mathbf{K}\neq\mathbf{H}}\frac{E(\mathbf{H}-\mathbf{K})\Phi(\mathbf{K})}{|\mathbf{H}-\mathbf{K}|^2}. \tag{29}$$

The last two equations can be used to upgrade the algorithm developed by Bethanis et al. [24] and play a key role to obtain relativistically valid *ab* initio crystal structure determination procedure. In fact, these equations can be regarded as alternative forms of the Dirac equation in connection with crystallographic notions. In the limit of $c \to \infty$ (non-relativistic limit), Eqs. (28) and (29) are reduced to key relations obtained from the Schrödinger equation [24].

4 Practical procedures and some illustrative results

The simplified spin-free one-component Dirac equations expressed in terms of crystallographic notions, Eqs. (27) and (28), are the basis formulae of the relativistic scheme. However, Eqs. (27) and (28) do not suffice to obtain a self-consistent scheme. For this purpose, it is reasonable that $E(\mathbf{H})$ is written as follows [24],

$$E(\mathbf{H}) = s\sum_{\mathbf{K}}\Phi(\mathbf{K})\Phi^*(\mathbf{K}-\mathbf{H}), \tag{30}$$

where s is a scale factor. Thus, Eqs. (27) and (28) form a self-consistent system to be solved by an iterative procedure with the aid of Eqs. (30).

Main principles of the algorithm developed by Bethanis et al. [24] were not changed. The moduli of the complex numbers E required for running these formulae were obtained from open-access diffraction data of a compound containing heavy elements and kept constant throughout the computations. Considerations related to crystallographic symmetry operations are not included in the calculations. Initial trial values of phases are introduced for a small subset of measured moduli of Es, and initial values for Φs are arbitrarily assigned to whole set of $\Phi(\mathbf{K})$. The values of $\Phi(\mathbf{H})$ prescribed by Eqs. (28) and (29) are recycled through two different routes. On the one hand, while they are introduced as $\Phi(\mathbf{K})$ of Eqs. (28) and (29) in the next cycle, on the other hand they are used in the right-hand entity of Eq. (30) in

Table 1 List of the five best-ranked solutions at α^4-accuracy level

Multisolution trial no.	No. of calculated phases	Mean phase errors (°)		
		Non-relativistic	Relativistic	
			ZORA	FORA
18	343	84,1	83.6	82.9
21	410	26,7	25.9	25.2
28	417	76,8	75.2	74.8
33	426	56,2	55.3	54.8
47	404	68,4	67.5	67.1

The other solutions have mean phase error (MPE) higher than 84°

order to generate new values of $E(\mathbf{H})$. In each cycle, only the phases of $E(\mathbf{H})$ are changed and new Es are calculated with the aid of Eq. (30), unless self-consistency between the consecutively obtained set of $E(\mathbf{H})$s is achieved, furthermore ZORA and FORA energy values without regard to electron correlation effects are recalculated in each cycle and subsequently inserted in Eqs. (28) and (29) for the next cycle.

The above theory at α^4-accuracy level was tested with a crystal structure previously reported [29], *cis*-(1,4-dithiane-S,S′)diiodoplatinum(II), which is crystallized in acentric space group $P4_32_12$, and the results regarding the compound were contrasted with non-relativistic ones in Table 1. To be able to compare the relativistic results with non-relativistic ones, the mean error between the calculated and correct phase prescribed by Eq. (26) was used. According to the results in Table 1, the relativistically calculated phases, of the observed set of Es are not considerably different from non-relativistic phases and the first ranked solution (MPE = 25.2°) approximately corresponds to correct values of phases. Furthermore, accuracy of the calculated phases increases as the order of regular approximation is raised. The most important result is also that the relativistic phase assignment procedure generates more precise values for the phases than those of its non-relativistic counterpart. As can be seen from Eq. (26), the phases of normalized structure factors are closely related to the atomic positions. Therefore, differences between the relativistic and the non-relativistic phase assignment procedure give rise to small changes in atomic positions. The electron density function on the $(1\bar{1}2)$ plane corresponding to the coordination plane of *cis*-(1,4-dithiane-S,S′)diiodoplatinum(II) [29], which is obtained from the Fourier transform of the set of $E(\mathbf{H})$s for which phase assignment is achieved with the FORA results of the best-ranked solution, is shown in Fig. 1. It is obvious that the electron density distribution corresponding to the best-ranked solution is sufficient to determine the atomic positions in the region of interest. However, in the presence of heavy atoms, it is not easy to determine positions of the light atoms such as hydrogen because of their small X-ray scattering factors as is in routine crystallographic studies.

In conclusion, the relativistic formulation presented here leads to an alternative way of crystal structure determination based on the Dirac equation. A notable advantage of this formulation is that it supplies a computational scheme having controllable accuracy level. Fine structure constant α controls accuracy level of the relativistic computation scheme. Although the formulation presented here has an accuracy level of α^4, it can be easily extended to relativistically higher accuracy levels. However, the present relativistic scheme cannot be used for precise experimental determination of ZORA and FORA eigenvalues because of the fact that electron correlation effects are overlooked for the sake of obtaining a tractable formulation.

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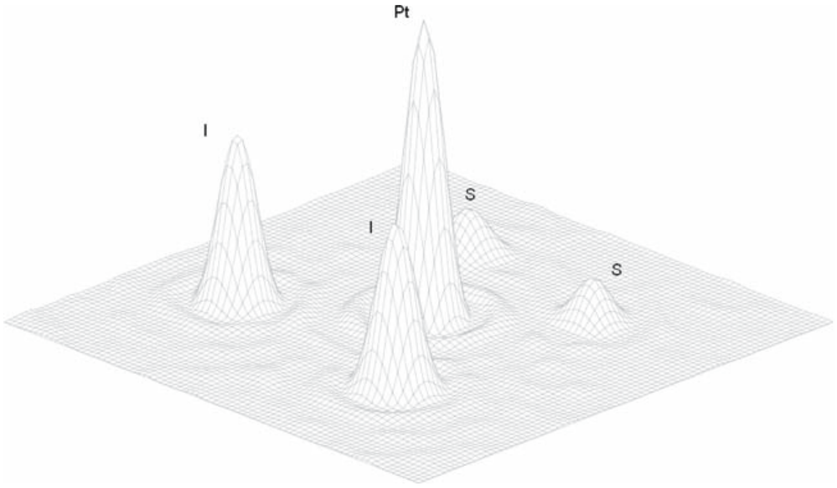

Fig. 1 Electron density function parallel to $(1\bar{1}2)$ plane with iso-surface level of 0.3 $e\text{Å}^{-3}$

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