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Ab initio determination of a crystal structure by means of the Schrödinger equation

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It is shown that the use of the Schrödinger equation may lead to the *ab initio* determination of the positions of the nuclei in a crystal, given a limited number of diffracted-beam intensities. In particular, it is shown that an extremely simplified Schrödinger equation in physical momentum space provides a sufficiently sound theoretical basis to develop an algorithm using diffraction data alone. This algorithm has been tested with a known 41 atom crystalline structure (not including hydrogen atoms) in space group $P1$. The extracted information is sufficient to determine the positions of all atoms. In addition, theoretical developments relevant to the connection between momentum space in quantum mechanics and diffraction theory have been formulated.

1. Introduction and goals

The time-independent Schrödinger equation is the usual basis of the *ab initio* determination of the multidimensional electronic wave function, given the nuclei positions. X-rays are scattered by electrons and the X-ray diffraction experiment on crystals provides a set of measured intensities of diffracted beams. The aim of this paper is to show that the use of the Schrödinger equation alone may also lead to the *ab initio* determination of the positions of the nuclei in a crystal, given a limited number of diffracted-beam intensities. In other words, we endeavour to *solve a simplified Schrödinger equation given a limited set of experimental diffraction intensities*, instead of the classical problem of solving this equation given the nuclei positions.[1] The solution will be achieved within a natural framework for this problem: the Schrödinger equation in physical momentum space, *i.e.* the space obtained by a Fourier transform (FT) operation on the usual position space. It is to be noted that for the present purpose we only wish sufficient precision to obtain from the electron-density map, *i.e.* $\rho = |\psi|^2$, approximate coordinates for the atoms of the crystal structure.

The determination of the atomic (nuclei) positions from the sole information of intensities of diffracted beams is known in crystallography as the 'solution of the phase problem'. This is the problem of determining the phases of the Fourier coefficients of the periodic electron-density function [equation (1) in §2], where only the moduli of these coefficients (structure factors) are provided by the diffraction experiment. The solution of the phase problem has been achieved by direct methods (DM) (Hauptman & Karle, 1953). The first noncentrosymmetric structure was solved by Karle & Karle (1964). Recently, a combination of phase-relation formulas with direct-space algorithms permits the determination of molecular structures with over 1000 atoms (Weeks *et al.*, 1994; Sheldrick, 1998; Burla *et al.*, 2000). We stress the fact that the present work does not use any one of the DM theoretical results. However, useful techniques such as the multisolution idea (Germain & Woolfson, 1968), which have been developed in the DM context, are also useful in the present *ab initio* determination of the nuclei positions by the Schrödinger equation.

2. Theoretical background

The present work is based upon an extreme simplification of the quantum-mechanical (QM) wave function. We consider that all electrons are independent of each other (no inter-electronic Coulomb repulsion), *i.e.* the potential function contains only the nuclei–electron attractive terms. Such an oversimplification is of course inappropriate for a satisfactory QM description of the wave function but it proves to be sufficient for achieving an acceptable approximation for the determination of the nuclei positions.

Thus, the electron density will be approximated by a one-electron quantum-mechanical *wave function* $\psi(\mathbf{r})$, with the obvious notations (FT for the Fourier transform):

$$\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2 \Leftarrow \mathrm{FT} \Rightarrow F(\mathbf{p}) = \varphi(\mathbf{p}) \otimes \varphi^*(\mathbf{p}), \qquad (1)$$

where $\otimes$ stands for the convolution operation and

$$\psi(\mathbf{r}) \Leftarrow \mathrm{FT} \Rightarrow \varphi(\mathbf{p})$$
$$\rho(\mathbf{r}) \Leftarrow \mathrm{FT} \Rightarrow F(\mathbf{p}).$$

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[1] Note that, if the phases of an infinite number of diffracted beams were known, this information would be strictly equivalent to the knowledge of the positions of the nuclei.

The moduli of the $F(\mathbf{p})$ values are obtained by the experimental diffraction intensities. The question arises then whether it is possible to obtain from fundamental quantum mechanics the unknown phases of $F(\mathbf{p})$ or, equivalently, the electron-density function $\rho(\mathbf{r})$, and finally the atomic positions. We show below that the electronic Schrödinger equation in Fourier (momentum) space provides a basis for such a determination (atomic units are used):

$$\begin{array}{ccc} \text{Direct space} & & \text{Momentum space} \\ -\Delta\psi(\mathbf{r})/2 + V(\mathbf{r})\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}) & \Leftarrow \text{FT} \Rightarrow & p^2\varphi(\mathbf{p})/2 + W(\mathbf{p}) \otimes \varphi(\mathbf{p}) = \varepsilon\varphi(\mathbf{p}) \end{array} \tag{2}$$

with $\quad V(\mathbf{r}) \Leftarrow \text{FT} \Rightarrow W(\mathbf{p})$.

For a periodic crystalline structure, the convolution integral is replaced by a discrete sum and equation (2) in momentum space is rearranged as equation (5).

Notation: We denote below by $\mathbf{H}$ (or $\mathbf{K}$) a reciprocal-lattice vector such that $\mathbf{H} = \mathbf{p}/2\pi = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$, where h, k, l are integers and $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ are the reciprocal unit-cell parameters. For simplicity, p^2, H^2, K^2 represent the squares of the respective vector lengths. The difference in the definition of FT in physics and mathematics (including crystallography) pertains to the factor 2π (see Appendix *A*). For convenience, we use throughout this paper the physics definition for continuous variables and the mathematical-crystallographic definition for discrete variables.

Thus, for $\mathbf{p} = 2\pi\mathbf{H}$, we have:

$$\begin{aligned} \varphi(\mathbf{p}) &= \varphi(2\pi\mathbf{H}) = (2\pi)^{-3/2}\Psi(\mathbf{H}) \\ W(\mathbf{p}) &= W(2\pi\mathbf{H}) = (2\pi)^{-3/2}\tilde{W}(\mathbf{H}). \end{aligned}$$

The next key remark is that the Fourier coefficients $W(\mathbf{p}) = W(2\pi\mathbf{H})$ of the potential function $V(\mathbf{r})$ are simply related to the normalized structure factors $E(\mathbf{H})$ defined in crystallography by:

$$E(\mathbf{H}) = \sum_j \frac{Z_j \exp(2\pi i\mathbf{H}\cdot\mathbf{r}_j)}{s_2} \quad \text{and} \quad s_2 = \left(\sum_j Z_j^2\right)^{1/2}, \quad j = 1, \ldots, N, \tag{3}$$

where N is the number of atoms in the unit cell and Z_j the atomic number of the jth atom.

We find that:

$$W(\mathbf{p}) = W(2\pi\mathbf{H}) = (2\pi)^{-3/2}\tilde{W}(\mathbf{H}) = -(2\pi)^{-3/2}\frac{s_2}{\pi H^2}E(\mathbf{H}). \tag{4}$$

Equation (4) is the *key relation* linking the quantum-mechanical potential function $W(2\pi\mathbf{H})$ to the complex amplitudes $E(\mathbf{H})$ of the diffracted beams by a crystal. Thus, (2) becomes, now with the discrete notation:

$$(2\pi H^2 - \varepsilon)\Psi(\mathbf{H}) = \frac{s_2}{\pi}\sum_K \frac{E(\mathbf{H}-\mathbf{K})\Psi(\mathbf{K})}{|\mathbf{H}-\mathbf{K}|^2}. \tag{5}$$

The electron energy ε is a negative quantity for bound states so that the first factor in the left part of (5) is always positive, and we can divide by it. This fact allows us to consider an iterative procedure to solve (5).

Furthermore, hydrogenoid atoms with spherical symmetry and quasi-point electron density (core electrons) are a satisfactory model for the present purpose. Thus, $F(\mathbf{p}) \propto E(\mathbf{H})$ and (1) is written as:

$$E(\mathbf{H}) = c\sum_{\mathbf{K}} \Psi(\mathbf{K})\Psi^*(\mathbf{K}-\mathbf{H}), \tag{1a}$$

where c is a scale factor easily determined. In any case, the passage from F's to E's is a well documented issue in DM bibliography.

The pair of equations (5) and (1*a*) form a system of self-consistent equations to be solved by iteration, which is a usual procedure in quantum mechanics.

It is important to emphasize that the Schrödinger equation written as (5*a*) has a form similar to that of a basic equation obtained by direct methods in crystallography (Karle & Hauptman, 1950; Hauptman & Karle, 1953; Sayre, 1952), equation (6):

$$\Psi(\mathbf{H}) = \frac{s_2}{\pi(2\pi^2H^2 - \varepsilon)}\sum_{\mathbf{K}} \frac{E(\mathbf{H}-\mathbf{K})\Psi(\mathbf{K})}{|\mathbf{H}-\mathbf{K}|^2} \qquad \text{Schrödinger equation} \tag{5a}$$

$$E(\mathbf{H}) = \sum_{\mathbf{K}} w(\mathbf{H},\mathbf{K})E(\mathbf{K})E(\mathbf{H}-\mathbf{K}) \qquad \text{direct methods,} \tag{6}$$

where $w(\mathbf{H},\mathbf{K})$ is a positive weighting factor evaluated by DM theory and complemented by semi-empirical considerations.

The physical meaning of this similarity is not discussed in this paper. We point out, however, that the Schrödinger equation is a postulate of quantum mechanics, while direct methods are mathematical theories based on physical assumptions such as the non-negativity of the electron-density function and the 'atomicity' property of real structures.

For the particular case of 'equal atoms' (N identical atoms with atomic number Z) and a wave function further simplified in the linear combination of atomic orbitals (LCAO) approximation (Berthier *et al.*, 1997), the similarity becomes a quasi-identity with the 'weighting' factor:

$$w(\mathbf{H},\mathbf{K}) = \frac{ZN^{1/2}}{\pi(2\pi^2H^2 - \varepsilon)}\frac{f^{\text{ato}}(\mathbf{K})}{f^{\text{ato}}(\mathbf{H})|\mathbf{H}-\mathbf{K}|^2}, \tag{6a}$$

where the function f^{ato} is the FT of atomic orbitals assumed identical for all atoms entering the LCAO expression with the same coefficients.

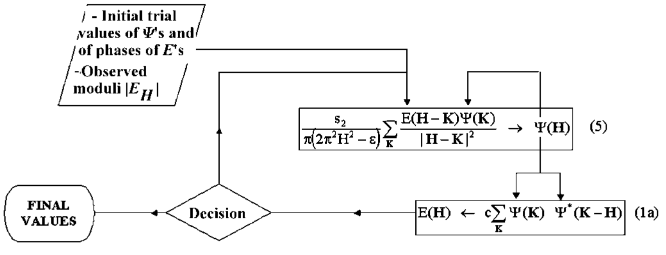

Figure 1
Flow chart of the algorithm.

Table 1
List of five trials of the multisolution procedure.

All others of the 64 multisolution results have MPE higher than 88°. It is clear that we have a unique solution for trial no. 22.

Multisolution trial no.	No. of calculated phases	MPE (°)
22	413	23.4
32	428	72.6
24	424	75.8
20	325	83.2
49	408	87.4

3. Practical procedures and testing of the algorithm

The simplified one-electron Schrödinger equation (5) is the basis formula of the procedure described in Fig. 1. Initial trial values for phases are introduced for a small subset of E's. Initial values for Ψ's are arbitrarily assigned to the whole set of $\Psi(\mathbf{K})$. Then the values $\Psi(\mathbf{H})$ obtained from (5) are recycled through two routes: directly by introducing them in the factor $\Psi(\mathbf{K})$ of (5) in the next cycle; indirectly by using them in the right-hand member of (1a) to produce new values of $E(\mathbf{H})$. In addition, in each cycle the total energy ε is recalculated and subsequently introduced in the left member of (5) by:

$$\varepsilon = \sum_{\mathbf{H}} 2\pi^2 H^2 \Psi(\mathbf{H})\Psi^*(\mathbf{H}) - \sum_{\mathbf{H}}\sum_{\mathbf{K}} \frac{s_2}{\pi}\frac{E(\mathbf{H}-\mathbf{K})\Psi(\mathbf{K})}{|\mathbf{H}-\mathbf{K}|^2}\Psi^*(\mathbf{H}).$$

An important remark should be made at this point. The moduli of the complex numbers E have been obtained from the diffraction experiment and are kept constant throughout the procedure. Only the phases $\phi(\mathbf{H})$ of $E(\mathbf{H})$ are changed in each cycle. In addition, new values of E's are obtained from (1a) beyond the initial trial subset. The phases $\phi(\mathbf{H})$ obtained from (1a) are introduced in the next cycle as phases $\phi(\mathbf{H}-\mathbf{K})$ of $E(\mathbf{H}-\mathbf{K})$ in the left-hand member of (5):

$$E(\mathbf{H}-\mathbf{K}) = |E_{\rm obs}(\mathbf{H}-\mathbf{K})|\exp[i\phi(\mathbf{H}-\mathbf{K})]. \qquad (5b)$$

The above algorithm has been tested with a known 41 atom crystalline structure,[2] not including hydrogen atoms, which crystallizes in the space group $P1$. We have used phases of three reflections fixing the origin in $P1$ and we have run the program with 64 initial trial values (this number stems from the usual algorithms where the phases of, for instance, three E's are set arbitrarily at $\pm\pi/4$; $\pm3\pi/4$).

In the general case of an unknown structure, each of the final results is to be tested by using discriminating criteria (Bethanis, Tzamalis, Hountas, Mishnev & Tsoucaris, 2000; Bethanis, Tzamalis, Hountas, Tsoucaris *et al.*, 2000) that will be discussed thoroughly in a forthcoming publication. Here we only mention that these criteria are based on the knowledge of the crystallographic symmetry, which however is not introduced in the calculations. Thus, progressive recovery of the symmetry in the course of iterations for each trial represents a criterion of correctness of the structure. In the present case with symmetry $P1$, the symmetry criterion could be replaced by a criterion pertaining to the Friedel phase relations. This has not been performed here and we have simply used the mean error between the calculated and the correct phases denoted by MPE (mean phase error). Table 1 shows the MPE for the five best rated solutions (out of 4^3). In the context of the present paper, it is important to show that only the first-ranked solution (MPE = 23.4°) *does lead to approximately correct values of phases of about 400 structure factors E(**H**)*; then common knowledge in crystallography ensures that this information is sufficient to determine the positions of all atoms in this 41 atom structure. As can be seen from Fig. 2, where for simplicity only one of the three molecules of the structure is drawn, the corresponding electron density for this solution reveals all the atomic positions.

It is to be noted that the idea of combining QM methods with experimental X-ray diffraction data has been used by Karle *et al.* (1998), in a context different from our present *ab initio* (in the crystallographic sense) problem. In this context, the use of crystallographic information facilitates quantum-mechanical calculations. There are circumstances such as structural complexity or alterations in structure from crystallization that are not conducive to structure determination by quantum-mechanical means. Combining the two fields of research allows additional information, *e.g.* electron densities, various energies and reaction paths, to be determined.

We state below two further theoretical developments relevant to the connection between momentum space in QM and diffraction theory.

4. Further theoretical developments

4.1. Phase invariance in the exact *n*-dimensional Schrödinger equation

For a bound state, the set of Ψ values that satisfies the extremely simplified one-electron Schrödinger equation (2) also satisfies the following relation:

$$\text{Phase of } \Psi = \text{Phase of } (W \otimes \Psi)$$
$$\Leftrightarrow \text{Phase of FT } [\psi(\mathbf{r})] = \text{Phase of FT } [V(\mathbf{r})\psi(\mathbf{r})]. \qquad (7)$$

It is worth noting that this momentum-space 'phase invariance' relation remains true for the exact multidimensional wave function, solution of the *complete electronic Schrödinger equation* including the inter-electronic repulsion.

The general equation (8) has been used in a previous publication by Navaza & Tsoucaris (1981) (N-T), aiming at the Hartree–Fock solution in momentum space of a system of n electrons moving in the potential field due to N nuclei:

$$\left(\sum_{i=1}^{n}\frac{p_i^2}{2}-\varepsilon\right)\varphi(\mathbf{p}_1,\ldots,\mathbf{p}_n)-\frac{1}{2\pi^2}\int \mathrm{d}\mathbf{q}\,\frac{s_2E(\mathbf{q})}{q^2}\sum_{i=1}^{n}\varphi(\mathbf{p}_1,\ldots,\mathbf{p}_i-\mathbf{q},\mathbf{p}_n)$$
$$+\frac{1}{4\pi^2}\int \mathrm{d}\mathbf{q}\,\frac{1}{q^2}\sum_{\substack{i,j=1\\ i\neq j}}^{n}\varphi(\mathbf{p}_1,\ldots,\mathbf{p}_i-\mathbf{q},\ldots,\mathbf{p}_j+\mathbf{q},\ldots,\mathbf{p}_n)=0, \qquad (8)$$

where the ith coordinate $\mathbf{p}_i$ is changed into $\mathbf{p}_i-\mathbf{q}$ and the jth coordinate into $\mathbf{p}_j+\mathbf{q}$.

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[2] 4,5-Bis(methylthio)-1,3-dithiol-2-ylium–bis(TCNQ), $C_{29}H_{15}N_8S_4$ (V. Psycharis, D. Mentzafos & A. Terzis, unpublished data)

The interpretation of (8) proposed by N-T is that the nuclear field potential transfers a momentum q to each electron in turn, thus changing the total momentum of the electronic system. The inter-electronic interaction does not change the total momentum but produces an inter-electronic momentum transfer between each pair of electrons in turn.

We stress now the fact that the phase invariance in the one-electron equation (7) also holds for the general exact Schrödinger equation (8) where the negative total energy $\varepsilon < 0$ for bound states implies that:

$$\sum_{i=1}^{n} (p_i^2/2 - \varepsilon) > 0.$$

Thus, we state that the phases of the eigenfunctions $\varphi(\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_n)$ of the exact electronic Schrödinger equation in momentum space for bound states are invariant under the convolution operator $W(\mathbf{p}) \otimes$. Rephrasing in n-dimensional coordinated space:

The phase of the Fourier transform of an eigenfunction $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$ of the exact electronic Schrödinger equation is, for bound states, invariant under the potential multiplication operator:

$$\begin{aligned}&\text{Phase of FT } [\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)]\\ &\quad = \text{Phase of FT } [V(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)]. \qquad (9)\end{aligned}$$

4.2. Expectation values in QM and crystallography

The quantity that expresses the physical 'observable' potential energy is obtained as an expectation value of the QM operator $V(\mathbf{r})$.

$$-e_{\rm pot} = -\langle\psi|V|\psi\rangle = -\textstyle\int \psi^*(\mathbf{r})V(\mathbf{r})\psi(\mathbf{r})\,{\rm d}\mathbf{r}. \qquad (10)$$

For a bound state, this quantity is positive, so the counterpart in momentum space,

$$-e_{\rm pot} = -(2\pi)^{-3/2} \textstyle\int {\rm d}\mathbf{p}\,\varphi^*(\mathbf{p}) \int {\rm d}\mathbf{q}\, W(\mathbf{p}-\mathbf{q})\varphi(\mathbf{q}), \qquad (11)$$

corresponds to a positive-definite Hermitian form.

In crystallographic notation, this means that

$$\sum_{\mathbf{H}}\sum_{\mathbf{K}} \frac{\Psi^*(\mathbf{H})E(\mathbf{H}-\mathbf{K})\Psi(\mathbf{K})}{|\mathbf{H}-\mathbf{K}|^2} \geq 0. \qquad (11a)$$

This relation recalls a well known fact in DM (Karle & Hauptman, 1950), *i.e.* the 'predominant positivity' of the 'origin invariants' (quantities that remain invariant under translation of the origin in direct space):

$$\mathrm{Re}[E^*(\mathbf{H})E(\mathbf{H}-\mathbf{K})E(\mathbf{K})]. \qquad (11b)$$

However, it is useful to emphasize that the probability concept used in DM is different from that of (10). In QM, the fundamental probability concept concerns $|\psi(\mathbf{r})|^2$. On the other hand, in crystallography the joint probability $p(E_1, E_2, \ldots)$ has been determined from first principles (Hauptman & Karle, 1953).

The connection between DM and quantum mechanics has been the subject of recent publications (Berthier *et al.*, 1996, 1997). This connection is obvious in the LCAO approximation leading to (6a). The evaluation of the expected value for an individual term (11b) is one of the basic results in DM theory. We note that the QM theory still provides a general indication concerning the predominance of positive terms (11a) and (11b).

5. Conclusions

In this work, we have used the Schrödinger equation in an unusual context: instead of the nuclei positions given *a priori*, we introduce into the algorithm a limited set of diffraction intensities. We have provided evidence that the iterative solution of the Schrödinger equation leads to an approximate wave function.

Moreover, this wave function is precisely located in the crystal lattice. Thus, the evaluation of the square of the wave function in position space, *i.e.* the electron-density function, leads to precise positions of all atoms within the unit cell. Clearly, this achievement provides a solution of the phase problem in crystallography, *i.e.* determination of the atomic positions from a limited set of diffracted intensities. It is interesting to note that the contribution in the fundamental equation (5) of terms that decay rapidly with increasing $|\mathbf{H}-\mathbf{K}|$ (because of the term $1/|\mathbf{H}-\mathbf{K}|^2$) has not been an obstacle for achieving the determination of the electron density at high resolution.

In the present paper, we have used a 41 atom structure to illustrate this new theoretical approach. Although modern calculation methods permit the determination of crystal structures with a number of atoms of the order of a thousand, the above structure is not a trivial case. The remarkable fact is that *an extremely simplified Schrödinger equation has provided a sufficiently sound theoretical basis to develop an algorithm using diffraction data alone*. Furthermore, the system of equations (1a) and (5) has enough power to address the practical problem stated in the introductory section, *i.e.* the *ab*

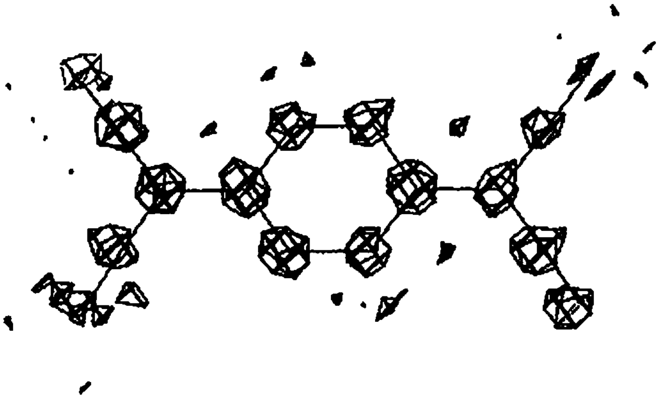

Figure 2
Electron-density map of one of the three molecules contained in the crystalline structure. The calculated electron-density function satisfactory determines all the atomic positions.

initio determination of atomic positions from the diffraction data alone.

Further developments include the combination of the present reciprocal- (momentum-) space algorithm with well known crystallographic procedures in direct space (*Shake-and-Bake*: Weeks *et al.*, 1994; *Half-Baked*: Sheldrick, 1998). The QM algorithm can be improved by using a Yukawa potential instead of the Coulomb potential. This can greatly enhance the high-resolution (large $|\mathbf{H}-\mathbf{K}|$) terms in (5) and it is expected to be better computationally adapted to atomic resolution problems.

APPENDIX *A*

We consider the following definitions of the Fourier transform (FT) of $\psi(\mathbf{r})$:

FT commonly used in physics:

$$\varphi(\mathbf{p}) = \mathrm{FT}[\psi(\mathbf{r})] = (2\pi)^{-3/2} \int \psi(\mathbf{r}) \exp(i\mathbf{p}\cdot\mathbf{r})\,\mathrm{d}\mathbf{r}; \qquad (12)$$

and FT used in mathematics and crystallography:

$$\Psi(\mathbf{H}) = \mathrm{FT}[\psi(\mathbf{r})] = \int \psi(\mathbf{r}) \exp(2\pi i\mathbf{H}\cdot\mathbf{r})\,\mathrm{d}\mathbf{r}. \qquad (13)$$

Equations (12) and (13) are related by setting $\mathbf{p} = 2\pi\mathbf{H}$:

$$\varphi(\mathbf{p}) = \varphi(2\pi\mathbf{H}) = (2\pi)^{-3/2}\Psi(\mathbf{H}).$$

The electron–nuclei attractive potential for N atoms of atomic number Z_j at positions $\mathbf{r}_j$ is (in atomic units):

$$V(\mathbf{r}) = -\sum_j Z_j |\mathbf{r}-\mathbf{r}_j|^{-1}. \qquad (14)$$

Then the FT of $V(\mathbf{r})$ is given respectively by the following expressions:

$$W(\mathbf{p}) = -\left(\frac{2}{\pi}\right)^{1/2} \sum_j \frac{Z_j \exp(i\mathbf{p}\cdot\mathbf{r}_j)}{p^2} \qquad \text{from (12)} \qquad (15)$$

$$\tilde{W}(\mathbf{H}) = -\frac{1}{\pi} \sum_j \frac{Z_j \exp(2\pi i\mathbf{H}\cdot\mathbf{r}_j)}{H^2} \qquad \text{from (13),} \qquad (16)$$

which are related by

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

By comparing (16) with (3), we see that

$$\tilde{W}(\mathbf{H})/E(\mathbf{H}) = -s_2/\pi H^2$$

and (4) follows.

A remarkable fact is that the potential term in momentum space bears only one singularity, and it is 'factorized' at the origin of momentum space as $1/H^2$, instead of presenting N singularities in direct space at each nucleus located at $\mathbf{r}_j$.

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