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Review Article

Probability Distributions of Phases I

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ABSTRACT

This article presents the mathematical foundation for calculating PD's (Probability Distributions) for some set of phases $\{\varphi h\}$ needed for the structure determination of a crystal. We can obtain PD's of the phases that can contain N or without N. A former paper could only obtain PD's of the phases containing N. Here we have the two possibilities.

Keywords: Random variable; Reciprocal vectors; Binomial distribution; Infinite number; Phase

INTRODUCTION

In a short review was given of the old probabilistic DM (Direct Methods) way for calculating phase distributions [1].

There were two mathematical approaches see (A) and (B) below

(A): The basic R.V.'s (Random Variables) are the set of the $X_i\,(1 \le i \ge N)$ that are distributed independently and uniformly over the asymmetric unit (we consider in this paper only P1) and one studies the normalized structure factors $E_h(X_{1,\ldots,}X_N)=\frac{1}{\sqrt{\sum f_i^2}}\sum_j f_{ie}{}^{2\pi i h.X_j}$

And one calculates the probabilities of the phases $\varphi h(\{X_i\})h$

(B): The basic R.V.'s are the reciprocal vectors h that are distributed uniformly and independently over reciprocal space and one keeps the X_i constant. This method can give algebraic equations as follows: One can study the structure factors E_h, E_{h+k} and we consider only h as the basic reciprocal vector and one keeps k fixed. The B_3,0 formula is an equation obtained this way. Although this equation gives the value of $cos(\varphi_h+\varphi_k-\varphi_{h+k})$ in theory, in practice this equation is wrong for high N, which is due to accidental overlap of the xi which invalidates the calculation of the joint probabilities of E_h and E_{h+k}. Even when one calculates the joint probabilities $P(E_h,E_k,E_{h+k})$ where h and k are the basic R.V.'s one must assume no accidental overlap of the xi (which becomes a problem for high N.). The calculation of joint probabilities gives then the same results as in (A) above.

(C): Using method (A) one can derive the probability of the cosine invariant $cos\varphi, \varphi \equiv \varphi_h+\varphi_k-\varphi_{h+k}$:

$$Prob(\varphi) \propto exp\left(2R_h,R_k,R_{h+k}\cos\varphi/\sqrt{N}\right)+O(1/N)$$

It follows that this formula

Loses predictive power for high N.

Cannot predict negative cosines.

The probabilities of quartets, quintets, etc. are even worse since they are of order of 1/N (for quartets), of order $1/N\sqrt{N}$ (for quintets), etc. (Although one can get a quartet formula that theoretically predicts negative cosines for the quartet (but again with too low predictive power)). At the end of the twentieth century nobody was busy anymore with calculating prob-abilistic phase distributions using one of the methods (A) or (B). For the calculations of structures with high N (N being here the number of independent non-H atoms in the asymmetric unit), one began to devise methods in direct space to solve crystal structures. One uses an automatic cyclical process: (a): Phase refinement (for instance with the use of the (modified) tangent formula) in reciprocal space and; (b): With the imposition in real space of physically meaningful constraints through an atomic interpretation of the electron density, with minimization of a well-chosen FOM (Figure Of Merit) of the phases. One of these methods in DM is known as the SnB (Shake and Bake) algorithm with N 1200 [2,3]; Another is the twin variables approach with $N \approx 1100$; Sir2000 the successor of SIR97 and SIR99 although different from SnB: (e.g. triplet invariants *via* the P10 formula with $N \approx 2000$. Another interesting result is the solution of a crystal when a substructure is known where N may become higher [4-9]. For an overview of DM before the year 2000 we refer to Giacovazzo [10].

(D): In order to circumvent these problems one approach might be to consider R.V.'s (x_i) that are no longer independent neither uniformly distributed, say a dependence through a positive distribution $\rho(\mathrm{x}_{1,\ldots,}\mathrm{x}_N)$.

One can give such distributions by using the functions $R_h(X_1,\ldots,X_N)$. But then one encounters insurmountable mathematical difficulties. The solution is to not consider the x_i as R.V.'s anymore but to replace $\rho(\mathrm{x}_{1,\ldots,}\mathrm{x}_N)$ by a field $\rho(x)$ and to sample the field over the allowable function space. What we shall discuss here is a novel way for doing DM (Direct Methods).

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(E): Differences with our approach

- We shall be able to solve any structure (any N) ab initio.
- Much lower CPU time.
- Let $e_1=(1,0,0)$, $e_2=(0,1,0)$, $e_2=(0,0,1,)$ and $h=(h_1,h_2,h_3)$, then with our approach we can easily calculate the probability distribution of $\varphi h-h_{1\varphi e_1}-h_{2\varphi e_2}-h_{3\varphi e_3}$ for any h. No need to compute all possible triplets.
- Easy to incorporate any given substructure.
- Easy to calculate the PD's (Probability Distributions) of phases: One only needs to take derivatives.

In this paper we shall give the mathematical basis that is necessary for this completely new DM approach. This approach is not mathematically as simple as in (A) and (B) but it is perfectly doable. It consists in using the atomic distribution function (x) as the basic random variable. The method will also be based on a functional integration over the random variable and using a nonstandard fuzzy approach wherein Dirac delta functions (among which a novel delta function representation for angle variables) are replaced by nonstandard fuzzy delta functions. To show the strength of the method, a simple formula was given in Brosius for the distribution of the triplet phase formula of the form $\Pr(\varphi)\propto e^{A\cos\varphi}$.

Where A is a function depending (not on N!) on the structure factors of the first neighborhood of the triplet [1].

In this paper a more profound mathematical foundation of our DM approach is given and this will be a major improvement compared to Brosius [1]. Recall that the sampling is done over positive functions $\rho:\mathrm{X}\in[0,1]^3\to R_+$ (in the space group P1) and that the R.V.'s that we study are the phases $\varphi h[\rho]$ which are defined by the relation

$$\exp(i\varphi h[p])\equiv\frac{1}{|F_h|}\int dXp(X)e^{2\pi ih.X} \quad \ldots\ldots (1)$$

Where is a R.V. defined by

$$F_h\equiv\int_X {}^{pXe^{2\pi ih.X}}$$

$$Fh=\sum_{k=1}^{N} f_{ke^{2\pi ih.X_k}}$$

and from now on we shall use the notations

$$F_h\equiv|F_h|$$

$$\kappa\equiv\langle|F_h|^2\rangle h\left(=\langle F_h^2\rangle h\right)$$

$$A_h\equiv|F_h|^2-k\left(=F_h^2-k\right)$$

One then needs to define a probability density $Pr[\rho]$ on the sample space ρ's. We build up $Pr[\rho]$ by fuzzy Dirac delta functions in 4 steps

Through constraints of the form $F[\rho]=F$ by using fuzzy Dirac delta's $\delta_\varepsilon\left(F[\rho]-F\right)$ (ε a positive infinitesimal).

Next through maximization: Adding obvious terms to $S[\rho]$ where $S[\rho]\equiv\ln Pr[\rho]$, that cannot be added by using a constraint, like e.g. the term.

$$\int\rho(x)D(x,y)\rho(y)D(y,z)\rho(z)D(z,x)dxdydz$$

Eventually we add fermionic terms to $S[\rho]$, like e.g.

$$\int\psi^*(x)\rho(x)D(x,y)\rho(y)\psi(y)dxdydz,$$

By imposing the mathematical requirement on the basic R.V. ρ that the different atoms in the unit cell of the crystal repel each other.

The idea is that if one would consider a function $\rho(x_1,\ldots,x_N)$ for which it is known that $\rho(\{X_i\})=0$ whenever x_i equals some x_j, this can be done by requiring that $\rho(x_1,\ldots,x_N)$ is antisymmetric in the x_i, that is

$$\rho(\ldots,X_i,\ldots,X_j,\ldots)=-\rho(\ldots,X_j,\ldots,X_i,\ldots)$$

Inspired by modern QFT (Quantum Field Theory) we replace $\rho(x_1,\ldots,x_N)$ by an antisymmetric (fermionic) field $\psi(X)$ with the property

$$\psi(X)\psi(y)=-\psi(y)\psi(X)$$

giving thus

$$\psi(X)^2=0$$

The added benefit is then that the different x_i will repel each other. Now one has two basic R.V.'s: ρ and ψ and we must integrate over ρ and ψ.

One can also sample over the set of Gaussian (normal) distributions by using the substitution

$$\rho(\mathrm{X})\to\rho(\mathrm{X})=\frac{1}{\sigma\sqrt{2\pi}}exp\left[-\frac{1}{2\sigma^2}\|\Delta\eta(\mathrm{X})-\Delta\bar{\rho}(\mathrm{X})\|^2\right]\ldots. (2)$$

where $\bar{\rho}(\mathrm{X})$ represents the true electronic distribution and $\Delta f(\mathrm{X})$ is the laplacian of f at the point x.

As in QFT, D (x, y) is called the propagator from the point y to x. Using constraints we shall see that the first candidate for D (x,y) is $Q(x-y)$ where Q is the origin-removed Patterson function defined here by

$$Q(\mathrm{X})\equiv\sum_{\mathrm{P}}(|F_{\mathrm{P}}|^2-\kappa)e^{-2\pi i\mathrm{P}\cdot\mathrm{X}}\equiv P(\mathrm{X})-\kappa\delta(\mathrm{X})\ldots. (3)$$

This propagator depends on N since $(|F_0|^2-\kappa)=\mathrm{O}(N^2)$.

LITERATURE REVIEW

Notations and formulas

$$f_{\mathrm{X}}=f(\mathrm{X})$$

$$\int_{\mathrm{X}}f_{\mathrm{X}}=\int f(\mathrm{X})d\mathrm{X} \text{ and } \int_{\mathrm{X},y,\ldots}f_{\mathrm{X},y,\ldots}=\int dxdy\ldots f(x,y,\ldots)$$

$$\int D\rho=\int\Pi_{\mathrm{X}}d\rho_{\mathrm{X}}$$

The error function $f(x)=\frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}dt$ [11,12]. We have then

$$erf(z)=\frac{2}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{(-1)^n z^{2n+1}}{n!(2n+1)}=\frac{2}{\sqrt{\pi}}e^{-z^2}\sum_{n=0}^{\infty}\frac{2^n z^{2n+1}}{(2n+1)!!}$$

$$\int_0^\infty dxe^{-ax^2-2bx}=\frac{\sqrt{\pi}}{2\sqrt{a}}e^{b^2/a}\left[1-erf\left(\frac{b}{\sqrt{a}}\right)\right]for\Re a>0$$

$$erf(-z)=-erf(z)$$

$$A_{\mathrm{P}}=|F_{\mathrm{P}}|^2-\kappa\left(=F_{\mathrm{P}}^2-\kappa\right)$$

$$F_{h,k}\equiv F_hF_kF_{h+k}$$

A without subscript stands for some infinite positive number.

$$P(x)=\Sigma_{\mathrm{P}}F_{\mathrm{P}}^2e^{-2\pi i\mathrm{P}\cdot\mathrm{X}}$$

$$Q(x)=\Sigma_{\mathrm{P}}\left(F_{\mathrm{P}}^2-\kappa\right)e^{-2\pi i\mathrm{P}\cdot\mathrm{X}}=p(\mathrm{X})-\kappa\delta(\mathrm{X})$$

$Q^{-1}(x-y)=\Sigma_P\left(F_P^2-\kappa\right)^{-1}e^{2\pi iP\cdot(x-y)+N-1}$, where $Q^{-1}(x-y)$ is the inverse of the kernel operator $Q(x-y)$.

The phase random variable $\varphi_P[\rho]$ is defined by $F_P e^{i\varphi_P[\rho]}=\int dX\rho(X)e^{2\pi iP\cdot X}$ where $\rho(x)$ denotes the atomic distribution and the function ρ is our basic R.V.

$f'g=\int_X f_X g_X$ and $\rho' Q\rho=\int_{x,y}\rho(x)Q_{x-y}\rho(y)$.

The functional integral

$$\int_{\rho\geq 0} D\rho\exp\left(-a\int_X \rho_X^2+2b\rho_x J_x\right)$$

$$=\prod_X\int_0^\infty d\rho_X\exp\left(-a\rho_X^2+2b\rho_x J_x\right)$$

$$\prod_X\frac{\sqrt{\pi}}{2\sqrt{a}}\left[1+erf\left(\gamma J_x\right)\right]\exp\left(\gamma^2 J_X^2\right)\left(where\,\gamma=\frac{b}{\sqrt{a}}\right)$$

$$\infty exp\left(\int_x In\left[1+erf\left(\gamma J_X\right)\right]+\gamma^2 J_X^2\right)\ldots.(4)$$

The b_n constants. We define the constants b_n by the series

$$In\left[1+erf\left(x\right)\right]=\sum_{n=1}^{\infty}\frac{b_n}{n=1}x^n$$

The bn;m constants, defined by

$$\left(\sum_{n=0}^{\infty}\frac{2^n z^{2n+1}}{(2n+1)!!}\right)^n=\sum_{m=0}^{\infty}b_{n,m}z^{n+m}$$

Our representation of $\delta(\varphi)$ for an angle φ is

$$\delta(\varphi)=\lim_{A\to\infty}\frac{1}{2\pi I_0(A)}e^{A\cos\varphi}$$

We then define the fuzzy nonstandard δ_A function by

$$\delta_A(\varphi)=\frac{1}{2\pi I_0(A)}e^{A\cos\varphi}$$

For real x (not an angle) we define the nonstandard fuzzy $\delta_\varepsilon(x)$ by

$\delta_\varepsilon(x)=\frac{1}{\sqrt{2\pi\varepsilon}}\exp\left(-\frac{x^2}{2\varepsilon}\right)$ for positive infinitesimal ε,

and for complex $z=x+iy$

$$\delta_\varepsilon(z)=\frac{1}{2\pi\varepsilon}exp\left(-\frac{|z|^2}{2\varepsilon}\right)$$

For some set H of reciprocal vectors we define

$$L_H(x)=\sum_{h\in H}\left(\frac{u_h}{F_h}+\upsilon_h F_h\right)\cos\left(\varphi_h-2\pi h\cdot x\right)$$

and sometimes we simply write $L_x=L_H(x)$.

We use the explicit definition of the functional derivative by

$$\frac{\delta F[\rho]}{\delta\rho(x)}=\lim_{\varepsilon\to 0}\frac{F[\rho+\varepsilon\delta_x]-F[\rho]}{\varepsilon},$$

Where

$$\delta_x(y)=\delta(x-y)$$

$$ln\,z=2\left(\left(\frac{z-1}{z+1}\right)+\frac{1}{3}\left(\frac{z-1}{z+1}\right)^3+\frac{1}{5}\left(\frac{z-1}{z+1}\right)^5+\ldots\right),$$

where $\Re z\geq 0, z\neq 0$

$$ln\,(z+a)=ln\,a+2\left(\left(\frac{z}{z+a}\right)+\frac{1}{3}\left(\frac{z}{z+a}\right)^3+\frac{1}{5}\left(\frac{z}{z+a}\right)^5+\ldots\right)$$

; Where $a>0,\Re z\geq -a, z\neq -a$

Some vector calculus: (f, g: vector valued functions, h a scalar function)

$$\nabla(f\cdot g)=(f\cdot\nabla)g+(g\cdot\nabla)f+f\times(\nabla\times g)+g\times(\nabla\times f)$$

$$\nabla(hf)=h(\nabla\cdot f)+f\cdot\nabla h$$

$$\nabla\times(f\times g)=f(\nabla\cdot g)-g(\nabla\cdot f)+(g\cdot\nabla)f-(f\cdot\nabla)g$$

$$\Delta=\nabla\cdot\nabla$$

$$\nabla(\nabla h\cdot\nabla h)=2(\nabla h\cdot\nabla)\nabla h+2\nabla h\times\left(\underbrace{\nabla\times\nabla h}_{=0}\right)$$

$$=2(\nabla h\cdot\nabla)\nabla h$$

Recall that in three dimensions $x=(x_1,x_2,x_3)$

$$\nabla_x=\left(\frac{\partial}{\partial x_1},\frac{\partial}{\partial x_2},\frac{\partial}{\partial x_3}\right)$$

$$\Delta_x=\frac{\partial^2}{\partial x_1^2},\frac{\partial^2}{\partial x_2^2},\frac{\partial^2}{\partial x_3^2}$$

Preliminary knowledge

For an introduction on nonstandard theory we refer to Diener et al. and for a more advanced text see Nelson [13,14].

Nonstandard theory: Standard numbers are the known numbers: $2,-1,\sqrt{2},\pi,\cdots$, the other numbers are the nonstandard real numbers which make up the field R. It is important to observe that there are an infinity of infinite numbers in R that are greater than any standard real number. Also there are an infinity of infinitesimals ε in R for which the absolute value $|\varepsilon|$ is less than any positive standard number in R. From the axioms it follows that for every positive infinitesimal $\varepsilon,\frac{1}{\varepsilon}$ is a positive infinite number and *vice versa*. Note that an infinite number is different from $\infty!$. In this paper we use A to denote an infinite positive number and ε will always denote (unless explicitly noted otherwise) a positive infinitesimal. ε_x or $\varepsilon(x)$ will denote a function that associates a positive infinitesimal with every position x in the unit cell $[0,1]^3$ $(in\rho 1)$. We will use this function in our fuzzy Dirac delta. $\delta_{\varepsilon_x}(\cdot)$ We shall use the notation $\delta_A(\cdot)$ instead of $\frac{1}{A}(\cdot)$ when we deal with angle variables.

Anticommuting variables: In a detailed exposition of anticommuting numbers is given [1]. In this subsection we shall only expose the bare minimum needed to read this paper. For more information, we refer to Weinberg, Siegel, Kuzenko et al. and for a more mathematical treatment to Bruhat et al. and deWitt [15-19].

One starts with a set of anticommuting numbers θ_λ:

$$\theta_\lambda\theta_\mu=-\theta_\mu\theta_\lambda\to\theta_\lambda^2=0$$

From this follows that every even product of such anticommuting numbers is commuting $(\theta_\lambda\theta_\mu\theta_\alpha\theta_\beta=\theta_\alpha\theta_\beta\theta_\lambda\theta_\mu)$. Also one adds the axiom: $z\theta_\lambda=\theta_\mu z,\forall z\in C$. Then the algebra $\wedge$ is defined as the set of all finite sums of products.

$$z\theta_1\theta_2\cdots\theta_M\,(z\in C, M\geq 0, all\theta_i different)$$

When M is even, this is a commuting number (also called even) and when it is odd it is an anticommuting number (also called odd). Sums of such products with even M do commute and are

called even, and with odd M these sums are anticommuting and are called odd. Every $z \in C$ is also even. It follows that every $\alpha \in \wedge$ is a sum $\alpha = \beta + \gamma$ with β even and γ odd. An involution $\alpha \to \alpha^*$ is defined such that, $\theta_\lambda^* = \theta_\lambda$ and $(\alpha\beta)^* = \beta^*\alpha^*, (z\alpha)^* = \overline{Z}\alpha^* = \alpha^*\overline{Z}$ for $z \in C$ and $(\alpha+\beta)^* = \alpha^* + \beta^*$ α^* is odd when α is odd and even when otherwise. One calls ψ or ψ_x an odd function of x if ψ_x is odd for every x. It then follows that $\psi_X^* \psi_X$ (or $\psi^*\psi$) is even. Then the derivative $\frac{\partial}{\partial\theta}$ with respect to the anticommuting variable θ is defined by

$\frac{\partial}{\partial\theta}\frac{\partial}{\partial\theta^*} = \frac{\partial}{\partial\theta^*}\frac{\partial}{\partial\theta}, i.e. \frac{\partial}{\partial\theta}$ is odd.

$\frac{\partial}{\partial\theta}\theta = 1$

$\frac{\partial}{\partial\theta}(f(\theta)+g(\theta)) = \frac{\partial}{\partial\theta}f(\theta) + \frac{\partial}{\partial\theta}g(\theta)$

$\frac{\partial}{\partial\theta}(a\theta) = -a\frac{\partial}{\partial\theta}\theta \left(= a\frac{\partial}{\partial\theta}\theta\right)$ When a is odd, (when a is even)

$\frac{\partial}{\partial\theta}(fg) = \left(\frac{\partial}{\partial\theta}f\right)g + (-1)^{\varepsilon(f)} f\frac{\partial}{\partial\theta}g$, where $\varepsilon(f) = 0$ for f even (=1 for f odd)

A function $f(\theta)$ of an odd variable θ has the simple form $f(\theta) = a + b\theta$ (Taylor expansion), (here a is odd when f is odd, and even otherwise, but b has the opposite statistics of f). This can be generalized for a function $f(\theta_1,...,\theta_N)$ of N anti-commuting variables: The coefficients of even products in the expansion of the θ_i have the same statistics as f , whereas the coefficients of uneven products have the opposite statistics. Next one defines the integration $\int d\theta$ as

$$\int d\theta f(\theta) = \frac{\partial}{\partial\theta} f(\theta),$$

and the multiple integration

$$\int d\theta_1 d\theta_2 .. d\theta_n = \int d\theta_1 \int d\theta_2 ... \int d\theta_n,$$

It is also convenient to define θ as an odd element: $d\theta_i d\theta_j = -d\theta_j d\theta_i$.

Also the following formulas are important

$\int zf(\theta)d\theta = z\int f(\theta)d\theta$ for constant z;

$\int d\theta f(\theta+\gamma) = \int d\theta f(\theta)$ for an odd constant γ

Note that the set of all odd numbers has vanishing volume

$\int d\theta \equiv 0$ and

$\int d\theta = -\int d\theta\theta = -1$

DISCUSSION

Determinants

The four determinants are listed below. The following Theoremes are:

Theorem 1: Let M be an $n \times n - matrix$. Then

$$\int d^n\theta d^n\theta^* \exp\left(\sum_{i,j}\theta_i^* M_{ij}\theta_j\right) = \det M$$

where by definition $\int d^n\theta d^n\theta^* \equiv \prod_{i=1}^n \int d\theta_i d\theta_i^*$

Proof develop $\exp\left(\Sigma_{i,j}\theta_i^* M_{ij}\theta_j\right)$ in sums of products of $\theta_i^*\theta_i$

$$\exp\left(\sum_{i,j}\theta_i^* M_{ij}\theta_j\right) = 1 + \sum_{ij}^n \theta_i^* M_{ij}\theta_j + ... + \theta_i^*\theta_i ... \theta_n^*\theta_n DetM$$

Since,

$\prod_{i=1}^n \int d\theta_i d\theta_i^* \left(\theta_i^*\theta_i ... \theta_n^*\theta_n\right) = 1$ the theorem follows.

The continuous version is as follows. Let $\psi(X)$ be an anticommuting variable for every X in the unit cell. Then,

$$\int D\psi(X) D\psi^*(X) \exp\left(\int dxdy\psi^*(x) M(x,y)\psi(y)\right) = Det\, M$$

where one has defined $D\psi(X) D\psi^*(X) \equiv \prod_X d\psi(X) d\psi^*(X)$

Theorem 2: Suppose now that the inverse M^{-1} exists and let $\eta(X)$ be an anticommuting variable for every X . Then

$$\int D\psi(X) D\psi^*(X) \exp\left(\psi^{*t} M\psi + \psi^{*t}\eta + \eta^{*t}\psi\right) = (\det M) e^{-\eta^{*t} M^{-1}\eta}$$

Where

$\psi^{*t} M\psi = \int_{x,y} \psi_X^* M_{X,y}\psi_y dxdy$

$\psi^{*t}\eta = \int_x \psi_X^*\eta_X d_X$

Proof let

$$Z_0[\eta^*,\eta] \equiv \int D\psi(X) D\psi^*(X) \exp\left(\psi^{*t} M\psi + \psi^{*t}\eta + \eta^{*t}\psi\right)$$

Then transform

$\psi \to \psi - M^{-1}\eta$

$\psi^* \to \psi^* - \eta^* M^{-1}$

and substitute this in $Z_0[\eta^*,\eta]$.Then using the relation $\int d\theta f(\theta+\gamma) = \int d\theta f(\theta)$

$$\int D\psi(X) D\psi^*(X) \exp\left(\psi^{*t} M\psi + \psi^{*t}\eta + \eta^{*t}\psi\right) = (DetM) e^{-\eta^{*t} M^{-1}\eta} \quad .... (5)$$

Thus

$$Z_0[\eta^*,\eta] = (DetM) e^{-\eta^{*t} M^{-1}\eta} \quad .... (6)$$

Also

$$\int D\psi(X) D\psi^*(X) f[\psi^*,\psi] \exp\left(\psi^{*t} M\psi + \psi^* t\eta + \eta^{*t}\psi\right)$$

$$= f\left[-\frac{\delta}{\delta\eta}, \frac{\delta}{\delta\eta^*}\right] Zo[\eta^*,\eta] .... (7)$$

The minus sign arises from the observation that $\psi^*\eta = -\eta\psi^*$ in

$$\exp\left(\psi^{*t} M\psi + \psi^{*t}\eta + \eta^{*t}\psi\right)$$

$$D_{x,y} = Q(x-y)$$

Indeed, note that

$$\int D\psi D\psi^*\psi(X)^* \exp\left(\psi^{*t} M\psi + \psi^{*t}\eta + \eta^{*t}\psi\right)$$

$$= \int D\psi D\psi^* \left(-\frac{\delta}{\delta\eta_X}\right) \exp\left(\psi^{*t} M\psi + \psi^{*t}\eta + \eta^{*t}\psi\right)$$

$$= \left(-\frac{\delta}{\delta\eta_X}\right) \int D\psi D\psi^* \exp\left(\psi^{*t} M\psi + \psi^{*t}\eta + \eta^{*t}\psi\right)$$

$$= \left(-\frac{\delta}{\delta\eta_X}\right) Z_o[\eta^*,\eta]$$

The probability functional $P_r[\rho]$

We shall show that we can obtain the following probability function $P(\{\varphi h\}\, h \in H)$ (H is some set of reciprocal vectors) given by $P(\{\varphi h\}\, h \in H) = \int_{\rho \geq 0} D\rho \Pr[\rho]$ .... (8)

where $\Pr[\rho]$ is given, up to a phase unimportant constant, by

$$\Pr[\rho] \propto \exp[S[\rho]]$$

$$S[\rho] = -a(\rho - \xi)^t(\rho - \xi) + b\int_X \rho_X D^{\xi}_{x,y}\rho y + c\rho^t L +$$

$$\sum_{P \neq 0} \alpha_P \left(\int_X \rho x e^{2\pi i P \cdot X} \int_X \rho x e^{-2\pi i P \cdot X} - F_P^2\right) +$$

$$\sum_{P \neq 0} \beta_P \left(\cos(\varphi_P[\rho] - \varphi_P) - 1\right) + -\frac{1}{4\gamma^2}\rho^t\rho + O[\rho^3]$$

$$L_X = cL_H(X) + f\int_z D_{X,z}\xi_z + \ldots$$

$$L_H(X) = \sum_{h \in H}\left(F_h + \frac{1}{F_h}\right)\cos(\varphi_h - 2\pi h \cdot X)$$

$$D^{\xi}_{x,y} = D_{x,y}\int_z D_{x,z}D_{y,z}\xi_z \text{ .... (9)}$$

where $z \to \xi_z$ denotes chemical information or an intermediate iteration of ρ.

$$\mathrm{Dx,\,y = Q\,(x - y\,)}$$

$Q(x-y)$ will be the basic operator for all our $D_{x,y}$. First we need the following theorem:

Theorem 3: Let $F[\rho]$ be a functional of ρ, such that $F[A\rho] = A^p F[\rho]$ where A is a positive infinite number and p an integer ≥ 1. If we impose the constraint

$$F[\rho] \equiv F(\{\varphi h\}\, h)$$

where F has the property that

$|F(\{\varphi h\}\, h)| = a$ constant (i.e. not depending on the phases φh).

Then if we define the action functional $S[\rho]$ by $\Pr[\rho] \equiv e^{s[\rho]}$ (where c>0 is a constant)

Then

$$S[\rho] = w_F \Re\left(F[\rho]F(\{\varphi h\}\, h)^*\right) + In(w_F)$$

$$(where\, w_F > 0). \text{ .... (10)}$$

For a sequence of such $F_k[\rho]$, $S[\rho]$ will become (if we drop the constant $In(w_F)$).

$$S[\rho] = \sum_k w_{F_k} \Re\left(Fk[\rho]F_k(\{\varphi h\}\, h)^*\right) \text{ .... (11)}$$

Proof we impose this constraint by

$$\Pr[\rho]\alpha\delta_{\in}(F[\rho] - F(\{\varphi h\}\, h))$$

$$\alpha\frac{1}{\in}\exp\left\{-\frac{1}{2\in}|F[\rho] - F(\{\varphi h\}\, h)|^2\right\}$$

$$\alpha\frac{1}{\in}\exp\left\{-\frac{1}{2\in}\left[|F[\rho]|^2 - 2\Re\left(F[\rho]F(\{\varphi h\}\, h)^*\right) + |F(\{\varphi h\}\, h)|^2\right]\right\}$$

Since $|F(\{\varphi h\}\, h)|$ is independent of the φh one can drop it in the above exponent. Next change $\rho = A^{-1}\eta$ and choose $\in = w_F^- A^{-p}$. Since $F[\rho] = F[A^{-1}\eta] = A^{-p}F[\eta]$, one obtains

$$\Pr[\rho] \to \Pr[\eta] \propto w_F A^p \exp\left\{-\frac{1}{2}\left[w_F \frac{A^{-2p}}{A^{-p}}|F[\eta]|^2 - 2w_F \frac{A^{-2p}}{A^{-p}}\Re\left(F[\eta]F(\{\varphi h\}\, h)^*\right)\right]\right\}$$

$$\propto w_F A^p \exp\left\{-\frac{1}{2}\left[w_F \frac{1}{A^{-p}}|F[\eta]|^2 - 2w_F\Re\left(F[\eta]F(\{\varphi h\}\, h)^*\right)\right]\right\}$$

$$\propto w_F A^p \exp\left\{w_F\Re\left(F[\eta]F(\{\varphi h\}\, h)^*\right)\right\}$$

since $\frac{1}{A^{-p}}|F[\eta]|^2 \approx 0$ (infinitesimal). Also under the change $\rho \to \eta = A\rho$ the integral volume $\int_{\rho \geq 0} D\rho \propto \int_{\rho \geq 0} D\eta$. So finally (after replacing η by ρ)

$$\int_{\rho \geq 0} D\rho \Pr[\rho] \propto \int_{\rho \geq 0} D\rho e^{S[\rho]}$$

$$S[\rho] = w_F\Re\left(F[\rho]F(\{\varphi h\}\, h)^*\right) + In(w_F)$$

$$= w_F\Re\left(F[\rho]F(\{\varphi h\}\, h)^*\right) \text{ (if we drop the constant In}\left(w_F\right)\text{)}$$

Theorem 4: One can write

$$S[\rho] = -\frac{1}{4\gamma^2}\rho^t\rho + c\rho^t L_H + \int_{x,y}\mu_{x-y}\rho_x Q_{x-y}\rho_y + \ldots \text{ .... (12)}$$

Where

$$\rho^t\rho \equiv \int \rho_x^2 dx \text{ .... (13)}$$

$$\rho^t L_H \equiv \int \rho_x L_H(x)dx \text{ .... (14)}$$

$$L_H(x) = \sum_{h \in H}\left(\frac{u_h}{IF_h} + \upsilon_h IF_h\right)\cos(\varphi_h - 2\pi h \cdot x) \text{ .... (15)}$$

$$Q_u \equiv \sum_p (IF_p^2 - k)e^{-2\pi i p \cdot u} \text{ .... (16)}$$

where from now on $\rho^t L_H$ is included $(!)$ in $S[\rho]$ for convenience, with parameters

$$u_h,\ \upsilon_h,\ \mu_u \geq 0 \text{ with } \mu_0 = 0.$$

$$D_{x,y} = Q(x - y)$$

Proof.

- Define $F[\rho] = \rho^t\rho$ and $F = \sum_P F_P^2$ and use the Dirac $\delta(F[\rho] - F)$. Then

$$\rho[\rho] \propto \delta(F[\rho] - F)$$

$$\propto e^{-\alpha F\delta}(F[\rho] - F)$$

$$= e^{-\alpha F[\rho]\delta}(F[\rho] - F)$$

$$\approx \exp(-aF[\rho] + w_F F[\rho]F)$$

$$= \exp\left(-\frac{1}{4\gamma^2}\rho^t\rho\right)$$

where we defined w_F such that $\frac{1}{4\gamma^2} = a - w_F F > 0$.

- The R.V. $\varphi h[\rho]$ was defined by $e^{i\varphi h[\rho]} \equiv \frac{1}{F_h}\int \rho(X)e^{2\pi i h \cdot x}dx$

Then the probability distribution of $\varphi h[\rho]$ is generated by the expression

$\Pr(\varphi_h) \equiv \int D\rho \Pr[\rho]\delta(\varphi h[\rho]-\varphi h)$.

But, (when A is infinite and positive)

$\delta_A(\varphi_h[\rho]-\varphi_h) \approx \frac{1}{2\pi I_0(u_h A)}\exp(Au_h\cos(\varphi h[\rho]-\varphi_h))$

$\propto \frac{1}{I_0(u_h A)}\exp(Au_h\cos(\varphi h[\rho]-\varphi h))$

$\propto \frac{1}{I_0(u_h A)}\exp\left(A\int_X p_x\left(\frac{u_h}{F_h}\cos(\varphi_h - 2\pi h\cdot X)\right)\right)$

After the transformation $\rho \to \eta = A\rho$ we obtain the result

$\delta_A(\varphi_h[\rho]-\varphi_h) \propto \frac{1}{I_0(u_h A)}\exp(\rho^t L')$

where $L' = \frac{u_h}{F_h}\cos(\varphi h - 2\pi h\cdot x)$. For convenience, from now on, we shall include $\rho^t L'$ in $S[\rho]$.

- Next use $F[\rho] = \int_X \rho_X e^{2\pi i h\cdot x}$ and $F = F_h e^{i\varphi h}$. Then

$S[\rho] = -\frac{1}{4\gamma^2}\rho^t\rho + \upsilon_h \Re(F[\rho]F^*) + \rho^t L'$

$= -\frac{1}{4\gamma^2}\rho^t\rho + \upsilon_h \Re\left(\int_X \rho_X e^{2\pi i h\cdot X}F_h e^{-i\varphi h}\right) + \rho^t L'$

$= -\frac{1}{4\gamma^2}\rho^t\rho + \int_X \rho_X\left(\frac{u_h}{F_h} + \upsilon_h F_h\right)\cos(\varphi_h - 2\pi h\cdot X)$

$= -\frac{1}{4\gamma^2}\rho^t\rho + \rho^t L_H$

where $L_H(X) = \left(\frac{u_h}{F_h} + \upsilon_h F_h\right)\cos(\varphi h - 2\pi h\cdot x)$.

- For every $X \in [0,1]^3$ we impose the constraint

$F_x[\rho] = Fx$

where

$F_x[\rho] \equiv \int_u \rho_x +_u \rho_u$

and

$F_x \equiv P(x)$

Then, according to theorem 1 above, one has

$S[\rho] = \ldots + \int dx\mu_x \int_u \rho_{x+u\ u}\,\mathrm{P(x)} + f[\mu] + \ldots$

$= \ldots + \int dx\,dy\mu_{x\ \_\mathrm{y}\ x} P(\mathrm{x}-y)\rho_y + \ldots (\mu_u \geq 0).$

Next note that there is a phase unimportant peak $\delta(\mathrm{x})$ at x = 0, and define Q by

$\mathrm{Q_x} = \mathrm{P(x)} - k\delta(\mathrm{x})$

$= \sum_p (\mathrm{F}_p^2 - k)e^{-2\pi i p\cdot x}$

Then if one chooses the positive function

$\mu : [0,1]^3 \to [0,\infty[$ *to satisfy* $\mu_0 = 0, \mathrm{S}[\rho]$ reads

$S[\rho] = \ldots + \int dx\,dy\,\mu_{x-y}\rho_x P(\mathrm{x}-\mathrm{y})\rho_y + \ldots$

$= \ldots + \int dx\,dy\,\mu_{x-y\rho x}Q(\mathrm{x}-\mathrm{y})_{\rho y} + \int_{x,y}\mu_{x\ \_y\rho x}\,\delta(\mathrm{x}-\mathrm{y})_{\rho y} + \ldots$

$= \ldots + \int dx\,dy\,\mu_{x-y\rho x}Q(\mathrm{x}-\mathrm{y})_{\rho y} + \mu_0\int dx\,\rho_x\rho_x + \ldots$

$= \ldots + \int dx\,dy\,\mu_{x-y\rho x}Q(\mathrm{x}-\mathrm{y})_{\rho y} + \ldots$

$= -\frac{1}{4\gamma^2}\rho^t\rho + \rho^t L_H + \int_{x,y}\mu_{x-y}\rho_x Q_{x-y}\rho_y + \ldots$

One can also add other terms to $S[\rho]$. For example consider the triplet expression

$F[\rho] = \int_{x,y,z}\rho_x\rho_y\rho_z \exp\left(2\pi i\left[h\cdot(x-z) + k\cdot(y-z)\right]\right)$

$F = F_h F_k F_{h+k}\exp(i\varphi)$ where $\varphi = \varphi_h + \varphi_k - \varphi_{h+k}$

Impose now the constraint $F[\rho] = F$. Since $F[A\rho] = A^3 F[\rho]$ and $|F|$ is constant in the phases we can write according to the basic theorem

$S[\rho] = \ldots + u_{h,k}F_{h,k}\int_{x,y,z}\rho_x\rho_y\rho_z\cos\left(2\pi\left[h\cdot(x-z) + k\cdot(y-z)\right] - \varphi\right) + \ldots$

where $u_{h,k} \geq 0$ and $\mathrm{F_{h,k}} \equiv F_h F_k F_{h+k}$ k. One can also do the same for quartets, quintets and so on. Next impose for the triplet, the constraint.

$\delta_{A^3}(\varphi[\rho]-\varphi) = \frac{1}{I_0(\upsilon_{h,k}A^3)}\exp\left[A^3\upsilon_{h,k}G[\rho]f_{h,k}\right]$

where

$G[\rho] = \int_{x,y,z}\rho_x\rho_y\rho_z$

$f_{h,k} = \frac{1}{F_h F_k F_{h+k}}\cos\left[2\pi\left[h\cdot(x-z) + k\cdot(y-z)\right] - \varphi\right]$

$\varphi[\rho] = \varphi_h[\rho] + \varphi_k[\rho] - \varphi_{h+k}[\rho]$

$\upsilon_{h,k} \geq 0$

Then $S[\ ]$ can finally be written (after $\rho \to A\rho$)

$S[\rho] = \ldots + \int_{x,y,z}\rho_x\rho_y\rho_z\left(u_{h,k}R_{h,k} + \frac{\upsilon_{h,k}}{R_{h,k}}\right)\times$

$\cos\left(2\pi\left[h\cdot(x-z) + k\cdot(y-z)\right] - \varphi\right) + \ldots$

Note that Important, $D_{x,y} = -\Delta_z Q_{z|\mathrm{z=x-y}} \equiv -\Delta_{\mathrm{x-y}}Q$ from now on we shall treat all weights $u_h = \upsilon_h = c$ the same: We shall not distinguish between the different measurements $|F_h|$. The same will be true for $\mu_x = b, \forall x$. The same is true for the $u_{h.k} : u_{h,k} = \upsilon_{h,k} = w$. But we shall not consider triplet terms of order $O\left[\rho^3\right]$ in this paper. So now we have arrived at

$S[\rho] = -\frac{1}{4\gamma^2}\rho^t\rho + b\int_x \rho_x Q_{x-y}\rho_y + cp^t L_H$ .... (17)

$\mathrm{D_{x,y}} = \mathrm{Q_{x-y}} - (\mathrm{F_0^2} - \mathrm{k})$

This propagator Dx,y does not depend anymore on $F_0^2 - k\left(= O\left(N^2\right)\right)\ \forall i, fi = f)$. In the sequel we shall simply say: "does not depend anymore on N". It is better than Q_{x-y}. Indeed to see this we can write $P[\rho]$] as

$P[\rho] \propto \int_{\rho\geq 0} D\rho\exp\left[b\int_{x,y}\rho_x D_{x,y}\rho_{y+\cdots}\right]$

$\propto \prod_x \int_o^\infty d\rho_x \exp\left(bp_x D_{x,y}\rho_y + \cdots\right)$ .... (18)

This last expression becomes very low whenever x-y is not an interatomic vector since then $Q_{x-y} = 0$ and thus

$D_{x,\mathrm{y}} = -\left(F_0^2 - k\right)$ and thus

$P(\rho) \propto \exp\left(-f^2 N^2\rho_x\rho_y\right)$

≈ 0

That is $P[\rho]\approx 0$ demoting such a ρ. We recall that we have also

$$S[\rho]=-\frac{1}{4\gamma^2}\rho^t\rho+b\int_{x,y}\rho_x D_{x,y}\rho_y+c\rho^t L_H \quad \text{.... (19)}$$

$$D_{xy} = -\Delta z Q_{z/z=x-y} \equiv -\Delta_{x-y} Q$$

Recall that $\Delta_x=\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial x_3^2}$ for $x=(x_1,x_2,x_3)$. In order to see what this new propagator can offer let us look at Q_x. Q_x is an N-sum of gaussian functions. Let us consider one of them, say $fx=\frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{1}{2\sigma^2}\|x-r\|^2\right)$. For sake of convenience we take now $r=0$ and we consider the one dimensional case $X=x$. Then $-\Delta_x=-\frac{d^2}{dx^2}$. And $h_x\equiv-\frac{d^2}{dx^2}f_x\propto\frac{1}{\sigma^3}\left(1-\frac{x^2}{\sigma^2}\right)f_x$. Thus at x=0 we see that h_x is $\frac{1}{\sigma^2}$ times larger than f_x since $h_x/f_x=\frac{1}{\sigma^2}$ which is very large since σ is very small. The function h_x then drops very fast to zero at $x=\sigma$ after which it remains negative, attains a negative minimum and then goes fast to 0 for $x\to\infty$. Also there is exactly one large negative minimum in the range $[-\infty<x<-\sigma]$ and one in the range $[\sigma<x<\infty]$. Exactly as discussed in $D_{x,y}=Q_{x-y}-(\mathrm{F}_0^2-\mathrm{k})$, $P[\rho]\approx 0$ for a ρ for which $\rho_X\neq 0$ at one of these minima. For

$$Q_X=\sum_{\mathrm{P}\neq 0}A_{\mathrm{P}}\exp(-2\pi i\mathrm{P}\cdot X) \quad \text{.... (20)}$$

we get

$$-\Delta_X Q_X=4\pi^2\sum_{\mathrm{P}\neq 0}A_{\mathrm{P}}\|\mathrm{P}\|^2\exp(-2\pi i\mathrm{P}\cdot X)$$

Because of the differentiation Δ_X this $D_{x,y}$ does not depend on N

Note, $D_{x,y}=\max(-\Delta_{x-y}Q,0)$. This $D_{x.y}$ can also be used; Then there are no negative minima, but in order to make it N independent, one has to follow the procedure used in $D_{x,y}=Q_{x-y}-(\mathrm{F}_0^2-\mathrm{k})$. That is we must subtract the term $\hat{D}_0$ in the Fourier expansion of $D_{x,y}$ to get a new propagator that is N-independent:

$$D_{x,y}=\hat{D}_0+\sum_{\mathrm{P}\neq 0}\hat{D}_{\mathrm{P}}e^{-2\pi i\mathrm{P}\cdot(x-y)}\to D_{new}(x,y)\equiv D_{x,y}-\hat{D}_0 \quad \text{.... (21)}$$

Improvements $D_{x,y}S_d(x-y)$

Let d be the maximum distance of all $\|r_i-r_j\|$ where r_j is the nearest neighbour of r_i. Then we can obviously replace the $D_{x,y}$ by $D_{x,y}S_d(x-y)$ where $S_d(u)$ is the characteristic function of the sphere $\{u\,\|\,u\|\leq d\}$ in the asymmetric unit of the crystal. Thus $\int_{x,y}\rho_x D_{x,y}\rho_y$ becomes $\int_{x,y}\rho_x D_{x,y}\rho_y S_d(x-y)=\int_{\|x-y\|\leq d}\rho_x D_{x,y}\rho_y$. If we know d we can then improve the phase densi- ties

$$D^{\xi}_{x,y} = D_{x,y}\int_z D_{x,z}D_{y,z}\xi_z \text{ with } L_x = cL_{H,x}+f\int_z D_{x,z}\xi_z$$

When ξ is a given chemical information (be it a submodel or an intermediate state of ρ during iteration) then we can derive a new propagator, with notation $D^{\xi}_{x,y}$, from $D_{x,y}$. Indeed if we look at the term $b\int_{x,y}\rho_x D_{x,y}\rho_y$ in $S[\rho]$ it is clear that we can consider an (improved) term $\int_{x,y}\rho_x D_{x,y}\rho_y D_{y,z}\rho_z D_{z,x}$ and replace $\int_{x,y}\rho_x D_{x,y}\rho_y$ with the latter term. For instance if $D_{x-y}=Q(X-Y)$ we see that $\int_{x,y,z}\rho_x D_{x,y}\rho_y D_{y,z}\rho_z D_{z,x}>0$ when and $x-y$ and $y-z$ and $z-x$ are interatomic vectors; This is a stronger restriction on than merely the condition $\int_{x,y}\rho_x D_{x,y}\rho_y>0$. Now if ξ is a submodel of ρ then we can also replace ρ_z by ξ_z and obtain again a term of order $\mathrm{O}[\rho^2]$ by replacing $\int_{x,y}\rho_x D_{x,y}\rho_y$ by the stronger condition (on ρ) $\int_{x,y,z}\rho_x D_{x,y}\rho_y D_{x,z}D_{y,z}\xi_z$ in $S[\rho]$. But now also L_x changes to $L_x=cL_{H,x}+b\int_z D_{x,z}\xi_z$. Indeed, in $b\int_{x,y}\rho_x D_{x,y}\rho_y$ we can replace ρ_y by ξ_y. Then cp^tL_H becomes p^tL where now $L_x=cL_H(\mathrm{x})+b\int_z D_{x,z}\xi_z$ in $S[\rho]$, (Remark that $D^{\xi}_{x,y}\equiv D_{x,y}\int_z D_{x,z}D_{y,z}\xi_z$ is symmetric whenever $D_{x,y}$ is), and we replace b by another parameter f. Hence for a given submodel ξ we can now write a better $[\rho]$:

$$S[\rho]=-\frac{1}{4\gamma^2}\rho^t\rho+b\int\rho_x D^{\xi}_{x,y}\rho_y+\rho^t L \quad \text{..... (22)}$$

with

$$L_x=cL_H(\mathrm{x})+f\int D_{x,z}\xi_z\,(f>0) \quad \text{..... (23)}$$

Example: We can always place the origin of the asymmetric unit wherever we want, i.e. we can always suppose that one atomic vector, say a, is given. This means that at least we can always use the chemical information.

$$\xi_x=f\delta(x-a) \quad \text{..... (24)}$$

Then we get

$$L_x=cL_H(x)+f\int_z Dx,a$$

$$D^{\xi}_{x,y}=D_{x,y}D_{x,a}D_{a,y} \quad \text{..... (25)}$$

Now we can show that with this we can directly calculate the density of the phase invariant.

$$\varphi_h-2\pi h\cdot a$$

instead of simply φ_h. Indeed consider the functional (where we write $D^a\equiv D^{\xi}$)

$$S[\rho]=-\frac{1}{4\gamma^2}\rho^t\rho+b\int\rho_x D^a_{x,y}\rho_y+\rho^t L$$

Next we do the functional change of variables: $\rho\to\eta$, where $\eta_x=\rho(\mathrm{x}+a)$. Then the Jacobian is the inverse of the determinant of the matrix $\frac{\partial\eta_x}{\partial\rho_y}=\delta(x-y+a)$ which is not dependent on the φ_h so $D\rho\alpha D\eta$. Then $S[\rho]$ changes to $S[\eta]$

$$S[\eta]=-\frac{1}{4\gamma^2}\eta^t\eta+b\int\eta_x D^a_{x+a,y+a}\eta_y+\int_x\eta_x L_x+a$$

$$D^{\xi}_{x,y}=D_{x,y}\int_z D_{x,z}D_{y,z}\xi_z \text{ with } \mathrm{L}_x=cL_{H,x}+f\int_z D_{x,z}\xi_z$$

and

$\mathrm{L}_{x+a}=cL_H(\mathrm{x}+\mathrm{a})+fD_{x+a,a}=\sum_{h\in H}(\frac{1}{F_h}+F_h)e^{i(\varphi h-2\pi h\cdot a-2\pi h\cdot x)}+fD_{x+a,a}$. Defining the phase invariant

$$\overline{\varphi h}\equiv\varphi h-2\pi h\cdot a$$

and considering the case that interests us most

$$D_{x,y} \equiv D_{x-y} \text{ ..... (26)}$$

we can write now

$$S[\eta] = -\frac{1}{4\gamma^2}\eta'\eta + b\int_{x,y}\eta_x D_{x-y} D_x D_y \eta_y + \int_x \eta_x L'_x$$

Where now

$$L'_x(\{\bar{\varphi}h\}\, h) \equiv L_{x+a} = c\sum_{h\in H}\left(\frac{1}{F_h} + F_h\right)e^{i(\bar{\varphi}h - 2\pi h\cdot x)} + fD_x \text{ ..... (27)}$$

Remark: $\bar{\varphi}h \equiv \varphi h - \pi h\cdot a$ is indeed a phase invariant because under a translation of the origin $x \to x+b$, also $(x,a) \to (x+b, a+b)$ and thus $\bar{\varphi}h \to \bar{\varphi}h$ under this translation which shows that $\bar{\varphi}h$ is indeed a phase invariant. For the reciprocal vectors $e_1 = (1,0,0)$, $e_2 = (0,1,0)$, $e_3 = (0,0,1)$ and $h = (h_1, h_2, h_3)$ we can write

$$2\pi h\cdot a = h\cdot\phi \equiv h_1\varphi_{e_1} + h_2\varphi_{e_2} + h_3\varphi_{e_3} \text{ ..... (28)}$$

where $a = (a_1, a_2, a_3)$ and $\varphi_{e_i} = 2\pi a_i$ and $\bar{\phi} = (\varphi_{e_1}, ..., \varphi_{e_3})$. So we can write the phase invariant $\bar{\varphi}h = \varphi h - h\cdot\bar{\phi}$ ..... (29)

The case for general ξ: Let $\hat{\xi}_p \equiv \int \xi(x)e^{2\pi i p\cdot x}$ and $\psi \equiv \arg(\hat{\xi})$ then

$$\xi(x) = \sum_p \left|\hat{\xi}_p\right| e^{i(\psi_p - 2\pi p\cdot x)} \text{ ..... (30)}$$

and consider

$$S[p] = -\frac{1}{4\gamma^2}\rho^t\rho + b\int \rho_x D^{\xi}_{x,y}\rho_y + \rho^t L$$

with $L_x = cL_x + f\int_z D_{x-z}\xi_z$. Then we apply the same functional change $\eta_x = \rho(x+a)$ and we then get for $S[\eta]$

$$S[\eta] = -\frac{1}{4\gamma^2}\eta^t\eta + b\int \eta_x D^{\xi'}_{x,y}\eta_y + \int_x \eta_x L'_x \text{ ..... (31)}$$

where

$$D^{\xi'}_{x,y} = D_{x-y}\int_z D_{x+a-z}D_{y+a-z}\xi_z$$

$$\int_z D_{x+a-z}D_{y+a-z}\xi_z = \int_z D_{x-z}D_{Y-Z}\xi_{z+a}$$

$$= \int_z D_{x-z}D_{y-z}\sum_p \left|\hat{\xi}_p\right| e^{i((\psi_p - 2\pi p\cdot a) - 2\pi p\cdot x)}$$

$$L'_x = cL'_x + f\int D_{x+a-z}\xi_z$$

$$= cL'_x + f\int_z D_{x-z}\xi'_z$$

$$L'_x(\{\varphi h\}) \equiv L_x(\{\bar{\varphi}h\}) \quad (\bar{\varphi}h \equiv \varphi h - 2\pi h\cdot a)$$

$$\xi'_z(\{\psi_p\}) \equiv \xi_z(\{\bar{\psi}_p\}) \quad (\bar{\psi}_p \equiv \psi_p - 2\pi p\cdot a)$$

$$2\pi h\cdot a \equiv h\cdot\bar{\phi} \text{ ..... (32)}$$

Note: From now on we shall always write $\bar{\varphi}h \equiv \varphi h - 2\pi h\cdot a$ instead of φh and $\bar{\psi}_p \equiv \psi_p - 2\pi p\cdot a$ instead of φh, resp. ψ_p in L_H, resp. ξ.

A fermionic action functional and a new $D_{x,y}$

One knows that the different atoms in the unit cell repel each other. So, our random variable ρ should be chosen in such a way that the different peaks of $\rho(x)$ spread over the unit cell and repel each other. This can be treated by considering ρ as an antisymmetric (fermionic) field written now as ψ. Then, following the treatment of QFT (Quantum Field Theory) [15], we replace.

$$\rho_x D_{x,y}\rho_y \to \psi^*_x D_{x,y}\psi_y$$

$$\rho_x L_x \to \psi^*_x L_x \delta(x-y)\psi_y \text{ ..... (33)}$$

Remark that $S[\rho]$ will be replaced by $S[\psi^*, \psi]$ which must be even and hermitian. So

$$S[\rho] = \rho^t D\rho + \rho^t L \to S[\psi^*, \psi] = \psi^{*t} D\psi + \psi^{*t}(L\psi)$$

$$\int D\rho e^{S[\rho]} \to \int D\psi D\psi^* e^{S[\psi^*,\psi]} \text{ ..... (34)}$$

Next

$$\int D\psi D\psi^* e^{S[\psi^*,\psi]} = \int D\psi D\psi^* e^{\psi^{*t}D\psi + \psi^{*t}(L\psi)}$$

$$= \det(D + LI)$$

$$I_{x,y} \equiv \delta(x-y) \text{ ..... (35)}$$

where I is the identity operator and we now replace $D_{x,y}$ by $D^{\xi}_{x,y}$. We then get (where $D^{\xi^{-1}}$ is the inverse of the operator D^{ξ}

$$\det(D^{\xi} + LI) = \det D^{\xi}\det(I + D^{\xi^{-1}}L)$$

$$\propto \det(I + D^{-1}L)$$

$$= \exp(Tr\ln(I + D^{\xi^{-1}}L)) \text{ ..... (36)}$$

since $\det D^{\xi}$ does not depend on the φh and since $\det X = e^{Tr\ln X}$ for a matrix X (Tr X is the trace of X, $TrX \equiv \int_x X_{x,x}$).

We can write

$$\ln(I + D^{\xi^{-1}}L) = D^{\xi^{-1}}L - \frac{1}{2}(D^{\xi^{-1}}L)^2 + \frac{1}{3}(D^{\xi^{-1}}L)^3 - \frac{1}{4}(D^{\xi^{-1}}L)^4 ...$$

$$D^{\xi^{-1}}L \equiv x \to \int_y D^{\xi^{-1}}_{x,y}L_y$$

$$Tr(D^{\xi^{-1}}L) = \int_x D^{\xi^{-1}}_{x,x}L_x$$

$$Tr(D^{\xi^{-1}}L)^2 = \int_{x,y} D^{\xi^{-1}}_{x,y}L_y D^{\xi^{-1}}_{y,x}L_x$$

$$Tr(D^{\xi^{-1}}L)^3 = \int_{x,y,z} D^{\xi^{-1}}_{x,y}L_y D^{\xi^{-1}}_{y,z}L_z D^{\xi^{-1}}_{z,x}L_x$$

Then using $L_x = cL_x + f\int_y D_{x,y}\xi_y$

$$Tr(D^{\xi^{-1}}L) = c\int_x D^{\xi^{-1}}_{x,x}L_x + f\int_x D^{\xi^{-1}}_{x,x}\int_Z D_{x,z}\xi_z \text{ ..... (37)}$$

$$Tr(D^{\xi^{-1}}L)^2 = \int_{x,y} D^{\xi^{-1}}_{x,y}(cL_y + f\int_z D_{y,z}\xi_z)D^{\xi^{-1}}_{y,x}(cL_x + f\int_z D_{x,z}\xi_z)$$

$$= c^2\int_{x,y} D^{\xi^{-1}}_{x,y}L_y D^{\xi^{-1}}_{y,x}L_x + 2fcD^{\xi^{-1}}_{x,y}L_y\int_z D_{y,z}\xi_z + C \text{ ..... (38)}$$

A fermionic action functional and a new $D_{x,y}$

Since $C \equiv f^2\int_{x,y} D^{\xi^{-1}}_{x,y}\int_z D_{y,z}\xi_z D^{\xi^{-1}}_{y,x}\int_z D_{x,z}\xi_z$ does not depend on the $\{\bar{\varphi}h\}\, h \in H$ we can dismiss it in equation (38). Next continue with the case "$D_{x,y} \equiv D_{x-y}$" and $D^{\xi}_{x,y} \equiv D_{x-y}\int_z D_{x-z}D_{x-z}\xi_z$, and we define

$$\hat{D}_p \equiv \int_{x,y} D_{x-y} e^{2\pi i p\cdot(x-y)}$$

$$B^{\xi}_{p,q} \equiv \int_{x,y} D^{\xi}_{x,y} e^{2\pi i(p\cdot x+q\cdot y)}$$

$$B^{\xi^{-1}}_{p,q} \equiv inverse\ of\ the\ matrix\ B^{\xi}\ at\ (p,q)$$

Then for $\xi_z = \sum_p \left|\hat{\xi}_p\right| e^{i(\bar{\psi}_p - 2\pi p\cdot z)}$ with $(\bar{\psi}_p \equiv \psi_p - p\cdot\bar{\phi} \equiv \bar{\psi}_p - 2\pi p\cdot a)$:

$$B^{\xi}_{h\ k} = \sum_p D_p D_{h-p} D_{h+k-p} \left|\hat{\xi}_{h+\ k}\right| e^{i\hat{\psi}_{h+k}}$$

$$D^{\xi^{-1}}_{x,y} = \sum_{p,q} B^{\xi^{-1}}_{p,q} e^{2\pi i(p\cdot x+q\cdot y)} \quad \text{..... (39)}$$

To get some idea let's consider the simpler case $D^{\xi}_{x-y} = Q_{x-y}$ but still $\mathrm{L}_x = cL_x + f\int_z D_{x-z}\xi_z$.

Then the inverse of Q, i.e. Q^{-1}reads

$$Q^{-1}_{x-y} = \sum_p A^{-1}_P e^{2\pi i p\cdot(x-y)}$$

Then

$$\ln\left(I+Q^{-1}L\right) = Q^{-1}L - \frac{1}{2}\left(Q^{-1}L\right)^2 + \frac{1}{3}\left(Q^{-1}L\right)^3 - \frac{1}{4}\left(Q^{-1}L\right)^4 + \ldots$$

$$Tr\left(Q^{-1}L\right) = \int_x Q^{-1}_{x-x} L_x$$

$$= Q_0^{-1}\int_x L_x = 0$$

$$Tr\left(Q^{-1}L\right)^2 = \int_{x,y} Q^{-1}_{x-y}\left(cL_y + f\int_z D_{y-z}\xi_z\right) Q^{-1}_{y-x}\left(cL_y + f\int_z D_{x-z}\xi_z\right)$$

$$= 2cf\left(\frac{1}{F_h} = F_h\right)\breve{A}_h \mid \xi_h \mid \cos\left(\varphi_h - \psi_h\right)\sum_p A^{-1}_p A^{-1}_{h-p} \quad \text{..... (40)}$$

Where we omitted a term in equation (40) that does not depend on φ_h. In equation (40) we have used the identities

$$D_{x-z} = Q_{x-y} - \left(F_0^2 - k\right) \equiv \sum_p \breve{A}_p e^{-2\pi i p\cdot(x-z)}$$

$$\left(\breve{A}_p = A_p\left(p \neq 0\right), \breve{A}_0 = 0\right)$$

$$\xi_z = \sum_p \mid \hat{\xi}_p \mid e^{i\left(\psi_p - 2\pi p\cdot z\right)}$$

$$L_x = \left(\frac{1}{F_h} + F_h\right)\cos\left(\varphi_h - 2\pi h\cdot x\right)$$

Finally, for $Tr\left(Q^{-1}L\right)^3$ we get (omitting the terms that don't depend on φ_h)

$$Tr\left(Q^{-1}L\right)^3 = 3fc^2\sum_p A^{-1}_p A^{-1}_{p-h} A^{-1}_{p-2h}\breve{A}_{2h} \mid \breve{\xi}_{2h} \mid \left(\frac{1}{F_h} + F_h\right)\cos\left(2\varphi_h - \psi_{2h}\right) +$$

$$3f^2 c\left(\frac{1}{F_h} + F_h\right)\sum_{k,p}\cos\left(\varphi_h + \psi_k - \psi_{h+k}\right) \mid \hat{\xi}_{h+k}\,\hat{\xi}_k \mid \breve{A}_k\breve{A}_{h+k} \times$$

$$A^{-1}_p A^{-1}_{p-h} A^{-1}_{p+h+k} \quad \text{..... (41)}$$

The terms $Tr\left(Q^{-1}L\right)^k \ \left(k \geq 4\right)$ are of higher order in f and c. So we see that we obtain in this way a probability of the form (remember $\bar{\varphi}_h \equiv \varphi_h - h\cdot\bar{\phi}$ and $\bar{\psi}_p \equiv \psi_p - p\cdot\bar{\phi}$, and thus $\bar{\varphi}_h - \bar{\psi}_h = \varphi_h - \psi_h$)

$$Pr\left(\varphi_h \mid \left\{\psi_p\right\}_p\right) \propto e^{A\cos\left(\varphi_h - \psi_h\right) + \sum_k B_k\cos\left(\varphi_h + \psi_k - \psi_h + k\right) + C\cos\left(2\varphi_h - \psi_{2h}\right)}$$

..... (42)

Equation (41) shows that for this model it is advantageous to choose f=c and then to use c for convergence considerations. For example, Equation (42) is then valid up to $O\left(c^4\right)$.

We can extend the above model and study instead the model with action.

$$S\left[\rho,\psi^*,\psi\right] = \left(\rho\psi^*\right)^t D^{\xi}\left(\rho\psi\right) + \left(\rho\psi^*\right)^t\left(L\psi\right) + \psi^{*t}\tilde{D}\psi + \rho^t D'_{x,y}\rho \quad \text{..... (43)}$$

To calculate then the functional integral $\int D\rho D\psi D\psi^* e^{S\left[\rho,\psi^*,\psi\right]}$ we use the following trick.

$$Z\left[J,\eta^*,\eta\right] \equiv \left|\int D\rho D\psi D\psi^* e^{S\left[\rho,\psi^*,\psi\right] + \rho^t J + \psi^{*t}\eta + \eta^{*t}\psi}\right| \quad \text{..... (44)}$$

If we then define

$$Z_0\left[J,\eta^*,\eta\right] \equiv \int D\rho D\psi D\psi^* e^{S_0\left[\rho,\mathrm{J},\psi^*,\psi,\eta^*,\eta\right]}$$

$$S_0\left[\rho,\psi^*,\psi,\eta^*,\eta\right] \equiv \psi^{*t}\tilde{D}\psi + \rho^t D'\rho + \rho^t J + \psi^{*t}\eta + \eta^{\ t}\psi$$

$$S_1\left[\rho,\mathrm{J},\psi^*,\psi,\eta^*,\eta\right] \equiv \left(\rho\psi^*\right)^t D^{\xi}\left(\rho\psi\right) + \left(\rho\psi^*\right)^t\left(L\psi\right)$$

Then

$$\int D\rho D\psi D\psi^* e^{S\left[\rho,\psi^*,\psi\right]} = \exp\left[\frac{\delta}{\delta J},\frac{\delta}{\delta\eta^*},-\frac{\delta}{d\eta}\right] Z_0\left[J,\eta^*,\eta\right]\mid_{J=\eta^*=\eta=0}$$

where the choice D^{ξ} is clear and where we choose $\tilde{D}_{x,y}$ and $D'_{x,y}$ to be of the form D_{x-y} and invertible to make calculations easier e.g. $\tilde{D}_{x-y} = D'_{x-y} = Q_{x-y}$. Let us define

$$W\left[J,\eta^*,\eta\right] \equiv \ln Z\left[J,\eta^*,\eta\right] \quad \text{..... (45)}$$

The it can be shown that $W\left[J,\eta^*,\eta\right]$ contains exactly all the connected diagrams of $Z\left[J,\eta^*,\eta\right]$[1,15,16]. It is beyond the scope of this article to talk more about diagrams, but we shall discuss it together with the solution in a future paper.

Averaging over gaussian distributions ρ

So far we have been averaging over all positive ρ in $\int_{\rho\geq 0} D\rho e^{S[\rho]}$. But what if we want to average only over gaussian ρ functions? The solution is the functional change of variables $\rho \to \rho = \delta\left(\eta - \bar{\rho}\right)$ where $\bar{\rho}$ is the true atomic distribution; This substitution is good if we don't care about N-dependence, if we don't want N-dependence we should instead consider $\rho = \delta\left(\Delta\eta - \Delta\bar{\rho}\right)$. That is $\rho_x = \delta\left(\Delta_x\eta - \Delta_x\bar{\rho}\right)$ ..... (46)

where η is a positive function, our new random variable.

Since $\bar{\rho}$ and thus also $\Delta_x\bar{\rho}$ is about the true density they are completely determined by the phases $\left\{\varphi_p\right\}_p$. In this way we will get a probability distribution of all φ_p. Then the "volume" element $D\rho$ is replaced by $D\eta\times\det\left(\frac{\delta\rho_x}{\delta\eta_y}\right)$, that is

$$\int D\rho \to \int_{\eta\geq 0} D\eta\det\left(\frac{\delta\rho_x}{\delta\eta_y}\right) \quad \text{..... (47)}$$

This can be calculated but we can avoid this added complexity if we remark that we could have started from the very beginning by using instead of ρ the more complex form $\delta(\Delta\eta-\Delta\bar{\rho})$ that is we replace ρL by $\delta\left(\Delta\eta-\Delta\bar{\rho}\right)L$ and so on. Replacing next the symbol η by ρ, we then get

$$\rho^t L\to\delta\left(\Delta\rho-\Delta\bar{\rho}\right)^t L$$

$$\rho^t D^\xi\rho\to\delta\left(\Delta\rho-\Delta\bar{\rho}\right)^t D^\xi\delta\left(\Delta\rho-\Delta\bar{\rho}\right),\ \text{..... (48)}$$

etc. In this way the former is now describing "point" particles. However, the whole use of functional integrals in QFT is to describe interactions among point particles. So we do not know if it is worth doing averages over those Gaussian "point" particles. We close this remark by giving two representations of the δ function. One is to represent $\delta\left(\Delta_x\eta-\Delta_x\bar{\rho}\right)$ by a gaussian with infinitesimal variance. The other very interesting representation is $\delta(a-b)=\frac{2}{\pi}\int_0^\infty xJ_0(ax)J_0[bx]dx$. In our case it reads

$$\delta\left(\Delta_x\rho-\Delta_x\bar{\rho}\right)=\frac{2}{\pi}\int_0^\infty kJ_0\left(k\Delta_x\rho\right)J_0\left(k\Delta_x\bar{\rho}\right)dk\ \text{..... (49)}$$

We can then first integrate over ρ and after that perform the integration over k, which is much easier.

Maximality with constraints

We saw in the foregoing sections that we had to maximize $S[\rho]=\mathrm{b}\,\rho^{\mathrm{t}}\,\mathrm{D}^\xi\,\rho+\mathrm{c}\,\rho^{\mathrm{t}}\,\mathrm{L}$. Let us analyze this further. We shall now start with

$$S[\rho]=-a(\rho-\xi)^t(\rho-\xi)+\mathrm{b}\,\rho^{\mathrm{t}}\,\mathrm{D}^\xi\,\rho+\mathrm{c}\,\rho^{\mathrm{t}}\,\mathrm{L}\ \text{..... (50)}$$

We will maximize this with the constraints $\left|\int\rho_x e^{2\pi ip\cdot x}\right|^2=F_P^2$ for all $\mathrm{P}\neq 0$ and $\varphi_{\mathrm{P}}[\rho]=\varphi_{\mathrm{P}}(\forall p\neq 0)$. Next observe that $\varphi_p[\rho]=\varphi_p\leftrightarrow\mathrm{COS}(\varphi_p[\rho]-\varphi_p)=1$. We then use the method of Langrangian multipliers. Put now

$$\tilde{S}[\rho,\alpha,\beta]\equiv S[\rho]-\sum_p\alpha_p\left(\left|\int\rho_{\mathrm{x}}e^{2\pi ip\cdot x}\right|^2-F_p^2\right)-\sum_p\beta_p(\cos(\varphi_p[\rho]-\varphi_p)-1)|$$

..... (51)

The minus signs in equation (51) have been chosen so as to use later on the more general "KKT- multipliers") and find the solutions $\rho^*,\alpha_{\mathrm{P}}^*,\beta_{\mathrm{P}}^*$ for which $\tilde{S}[\rho,\alpha,\beta]$ is maximal (critical), that is solve the equations

$$\frac{\delta}{\delta\rho}\tilde{S}[\rho,\alpha,\beta]=0$$

$$\frac{\partial}{\partial a_p}\tilde{S}[\rho,\alpha,\beta]\equiv 0$$

$$\frac{\partial}{\partial b_p}\tilde{S}[\rho,\alpha,\beta]\equiv 0\quad\text{..... (52)}$$

Next

$$\frac{\delta}{\delta\rho_{\mathrm{x}}}\tilde{S}[\rho,\alpha,\beta]=-2a(\rho-\xi)_x+2bD_x^\xi\rho+cL_x+2\sum_p\alpha_p\int_y\rho_y e^{2\pi ip\cdot(x-y)}+\sum_p\beta_p\frac{\delta}{\delta\rho_x}\cos(\varphi_p[\rho]-\varphi_p)=0$$

..... (53)

$$\frac{\partial}{\partial\alpha_p}\tilde{S}[\rho,\alpha,\beta]=\int_{x,y}\rho_x\rho_y e^{2\pi ip\cdot(x-y)}-F_p^2=0$$

$$\frac{\partial}{\partial\beta_p}\tilde{S}[\rho,\alpha,\beta]=(\cos(\varphi_p[\rho]-\varphi_p)-1)=0\ \text{..... (54)}$$

Next observe that

$$\cos(\varphi_p[\rho]-\varphi_p)=\frac{1}{F_p}\int_x\rho_x\cos(2\pi p\cdot x-\varphi_p)\left(\equiv\frac{1}{F_p}\rho^t\eta_p\right)$$

$$\frac{\delta}{\delta\rho_x}\cos(\varphi_p[\rho]-\varphi_p)=\frac{1}{F_p}\cos(2\pi p\cdot x-\varphi_p)$$

$$D_{\mathrm{X}}^\xi\rho\equiv\int_y D_{x,y}^\xi\rho_y\ \text{..... (55)}$$

Since L_H in $L\equiv L_H+fD\xi$ has now become redundant, we replace cL by $fD\xi$ in equation (51). We can also add inequality constraints for ρ

$$\rho^t D\xi\geq 0$$

$$f\geq 0\ \text{..... (56)}$$

and

$$\rho^t D^\xi\rho\geq 0$$

$$b\geq 0\ \text{..... (57)}$$

In this case the multipliers α_p,β_p,f,b are called KKT-multipliers (KKT stands for Karush- Kuhn-Tucker). And we have a dependence $S\equiv[\rho,\alpha,\beta,f,\mathrm{b}]$ now on ρ,α,β,f,b

$$S\equiv-a(\rho-\xi)^t(\rho-\xi)+\mathrm{b}\,\rho^t D^\xi\rho+f\rho^t D\xi-\sum_p\alpha_p\left(\int_{x,y}\rho_x\rho_y e^{2\pi ip\cdot(x-y)}-F_P^2\right)-\sum_h\beta_h(\cos(\varphi_h[\rho]-\varphi_h)-1)+f\rho^t D\xi$$

..... (58)

It follows from the above equation that we can impose (we suppose in this paper that friedel's law is valid, that is $F_{-h}=F_h$ and $\varphi_{-h}=-\varphi_h$):

$$\alpha_{-p}=\alpha_p$$

$$\beta_{-h}=\beta_h$$

We use the notation A^{t} to denote the transpose of A, and then $\mathrm{C}_p^t=C_{-p}$. We have to solve

$$\frac{\delta}{\delta_\rho}S=0$$

$$\frac{\partial}{\partial\alpha_\rho}S=$$

$$\frac{\partial}{\partial\beta_\rho}S=0$$

$$\frac{\partial}{\partial f}S=0$$

$$\frac{\partial}{\partial b}S=0\quad\text{..... (59)}$$

We find

$$\frac{\delta}{\delta\rho^*}S=-2a\rho^*+2a\xi+2bD^\xi\rho+fD\xi-2\sum_p\alpha_p C_p\rho^*-\sum_h\beta_h\frac{1}{F_h}\eta_h=0$$

This gives (using ρ^* instead of ρ)

$$D\rho = 2a\xi - \sum_h \beta \frac{1}{F_h}\eta_h + fD\xi \;\&\; \left(D \equiv 2aI - 2bD^{\xi} + 2\sum_P \alpha_p C_p \right) \text{..... (60)}$$

and thus

$$\rho = D^{-1}\left(a\xi + cL - \sum_h \beta_h \frac{1}{F_h}\eta_h \right) \text{..... (61)}$$

Next we develop D^{-1}, using Siegel [16]

$$\frac{1}{A+B} = \frac{1}{A} - \frac{1}{A}B\frac{1}{A} + \frac{1}{A}B\frac{1}{A}B\frac{1}{A} - \ldots \text{..... (62)}$$

$$A = 2aI - 2bD^{\xi}$$

$$B = \sum_p 2\alpha_p C_p \text{..... (63)}$$

Then,

$$D^{-1} = \frac{1}{A} - \frac{1}{A}B\frac{1}{A} + \frac{1}{A}B\frac{1}{A}B\frac{1}{A} + \ldots$$

Then we can write if we choose a to be great and b small $(a >> b)$

$$A^{-1} = -(2b)^{-1} D^{\xi-1}\left(-\frac{a}{b}D^{\xi-1} + I \right)^{-1}$$

$$= (2a)^{-1}\left(I + \frac{1}{a}D^{\xi} + \left(\frac{b}{a}\right)^2 \left(D^{\xi}\right)^2 + O\left(a^{-3}\right) \right) + O\left(a^{-4}\right) \text{..... (64)}$$

or if we choose a small and $(b >> a)$

$$A^{-1} = -\left(2bD^{\xi}\right)^{-1}\left(-\frac{a}{b}\left(D^{\xi}\right)^{-1} + I \right)^{-1}$$

$$= -(2b)^{-1} D^{\xi-1}\left(\mathrm{I} + \frac{a}{b}D^{\xi-1} + \left(\frac{a}{b}\right)^2 (D^{\xi-1})^2 + O(\mathrm{b}^{-3}) \right) \text{..... (65)}$$

Since we prefer to use the easier D^{ξ} instead of $\left(D^{\xi}\right)^{-1}$ we shall in this paper proceed with the development of equation (64). Then for $a >> b$ we find

$$\rho^* = \xi + (2a)^{-1}\left(2bD^{\xi}\xi + fD\xi - \sum_h \beta_h \frac{1}{F_h}\eta_h \right) - a^{-1}\left(\sum_p \alpha_p C_p \right)\xi + O\left(a^{-2}\right) \text{..... (66)}$$

Next $\frac{\partial}{\partial \beta_h} S = 0$ gives

$$\cos\left(\varphi_h[\rho] - \varphi_h\right) - 1 = 0$$

$$\frac{1}{F_h}\rho^t \eta_h = 1$$

$$\sum_p 2\alpha_p \left(C_p\xi\right)^t \eta_h + \beta_h \frac{1}{F_h} = 2a\left(\xi^t\eta_h - F_h\right) + \left(2b\eta_h^t D^{\xi}\xi - f\eta_h^t D\xi\right) \text{..... (67)}$$

Next $\frac{\partial}{\partial \alpha_p} S = 0$ will give (note $\{A,B\} \equiv AB + BA$)

$$\alpha_p = \frac{a}{2}\left(1 - \frac{F_p^2}{\left|\xi_p\right|^2} \right) - \beta_p \frac{1}{4F_p\left|\xi_p\right|}\cos\left(\varphi_p - \psi_p\right) + \frac{f\xi^t\{D,C_p\}\xi}{2\left|\xi_p\right|^2} + \frac{b\xi^t\{D^{\xi},C_p\}\xi}{2\left|\xi_p\right|^2} \text{..... (68)}$$

From $\frac{\partial}{\partial f} S = 0$ follows

$$f = \frac{\sum_h \beta_h \frac{1}{F_h}\eta_h^t D\xi + \sum_p 2\alpha_p \left(C_p\xi\right)^t D\xi - 2a\xi^t D\xi - 2b\left(D^{\xi}\xi\right)^{\xi} D\xi}{\left(D\xi\right)^t D\xi} \text{..... (69)}$$

From the equations (67,68) we derive the values of α_p and β_p as functions of f and b. From these results and equation (69) we derive the value of f as a function b. We now see that α_p, β_p, f are of order $O(a)$. If we would derive the value for b with the condition $\frac{\partial}{\partial b} S = 0$ then we will also see that b is of order $O(a)$ which gives a problem since we started with the assumption $(a >> b)$. For this reason, we shall not impose the condition $\rho^t D^{\xi}\rho \geq 0$. The bare minimum is the calculation of all the Lagrange multipliers α_p and one or more Lagrange multipliers β_h. All the multipliers depend strongly on the phase invariants $n\left(\varphi_p - \psi_p\right)(n = 1,2)$ The situation becomes even more interesting if one now calculates $S\left[\rho^*, \alpha^*, \beta^*, f^*\right]$ and this is good news. We think that this last model is very exciting (perhaps it can even be used to construct the exact ρ from any given ξ). We will study all this in a separate paper. Now $S\left[\rho, \alpha^*, \beta^*, f^*\right]$ can be written in a short way as

$$S\left[\rho, \alpha^*, \beta^*, f^*\right] = S\left[\rho^*, \alpha^*, \beta^*, f^*\right] + \left(\rho - \rho^*\right)^t S''[\rho]\left(\rho - \rho^*\right) \text{..... (70)}$$

Since $S'\left[\rho, \alpha^*, \beta^*, f^*\right] \equiv 0$ and moreover one can verify easily that $S''[\rho]_{x,y} = 2be^{2\pi ip\cdot(x-y)}$ is a constant in ρ.

CONCLUSION

To calculate a probability distribution prob (φ_h) for some phase φ_h one chooses one of the models discussed in this paper and also some set $H \ni h$ of reciprocal vectors containing h. Then one calculates $\Pr\left(\{\varphi_p\}_{p\in H}\right)$ according to the chosen model. After that one calculates the marginal distribution $prob(\varphi_h) = \int \prod_{p\neq h} d\varphi_p \Pr\left(\{\varphi_p\}_p\right)$. Always choose structural information ξ e.g. the fixing of the origin $\xi_x \propto \delta(x - a)$. All models should lead to the solution of the phase problem.

In a future paper (II) we shall study in detail all different models but especially the fermionic model and the one of maximality with constraints. Especially we shall discuss the most general fermionic model $S\left[\rho, \psi^*, \psi\right]$ and we shall talk about the technique of the diagrams to calculate $W\left[J, \eta, \eta^*\right] = \ln Z\left[J, \eta, \eta^*\right]$.

For the very interesting model of maximality with constraints we shall also add the KKT condition $\rho \geq \xi$ with some KKT multiplier $\gamma \geq 0$. Finally, in a last paper (III or IV) we shall test the theory on simulated crystal structures.

We shall also discuss which strategy to use in case of available space group information. Our paper treated only the space P1 (satisfying Friedel's law). Our use of functional integration and calculus is much more powerful than the other methods of phase determination, be it probabilistic or direct space methods and is valid for any number N of atoms. We shall also try to discuss models for which the formulas will depend N.

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