

7. Direct Methods

Electron density squared

We can write the electron density of a crystal as a Fourier series:

$$\rho(\mathbf{r}) = \frac{1}{v} \sum_{\mathbf{H}} F_{\mathbf{H}} \cdot e^{-2\pi i \mathbf{r}_{\mathbf{H}}^* \cdot \mathbf{r}}$$

Can we say anything about the function $g(\mathbf{r}) = \rho^2(\mathbf{r})$?

$$g(\mathbf{r}) = \frac{1}{v^2} \sum_{\mathbf{H}, \mathbf{H}'} F_{\mathbf{H}} \cdot F_{\mathbf{H}'} \cdot e^{-2\pi i (\mathbf{r}_{\mathbf{H}}^* + \mathbf{r}_{\mathbf{H}'}^*) \cdot \mathbf{r}}$$

Define $\mathbf{H}'' = \mathbf{H} + \mathbf{H}'$, which gives $\mathbf{r}_{\mathbf{H}''}^* = \mathbf{r}_{\mathbf{H}}^* + \mathbf{r}_{\mathbf{H}'}^*$. Then $\mathbf{H}' = \mathbf{H}'' - \mathbf{H}$.

Its Fourier transform is

$$\begin{aligned} g(\mathbf{r}) &= \frac{1}{v^2} \sum_{\mathbf{H}, \mathbf{H}'} F_{\mathbf{H}} \cdot F_{\mathbf{H}'' - \mathbf{H}} \cdot e^{-2\pi i \mathbf{r}_{\mathbf{H}''}^* \cdot \mathbf{r}} \\ &= \frac{1}{v} \sum_{\mathbf{H}''} \left(\frac{1}{v} \sum_{\mathbf{H}} F_{\mathbf{H}} \cdot F_{\mathbf{H}'' - \mathbf{H}} \right) \cdot e^{-2\pi i \mathbf{r}_{\mathbf{H}''}^* \cdot \mathbf{r}} \\ &= \frac{1}{v} \sum_{\mathbf{H}} \left(\frac{1}{v} \sum_{\mathbf{H}'} F_{\mathbf{H}'} \cdot F_{\mathbf{H} - \mathbf{H}'} \right) \cdot e^{-2\pi i \mathbf{r}_{\mathbf{H}}^* \cdot \mathbf{r}} \\ g(\mathbf{r}) &= \frac{1}{v} \sum_{\mathbf{H}} G_{\mathbf{H}} \cdot e^{-2\pi i \mathbf{r}_{\mathbf{H}}^* \cdot \mathbf{r}} \end{aligned}$$

So

$$G_{\mathbf{H}} = \frac{1}{v} \sum_{\mathbf{H}'} F_{\mathbf{H}'} \cdot F_{\mathbf{H} - \mathbf{H}'}$$

We have shown that $\rho^2(\mathbf{r})$ can be represented as a Fourier series with the same periodicity as $\rho(\mathbf{r})$, and that its Fourier components can be related to those of $\rho(\mathbf{r})$.

Properties of electron density squared

Let's assume that atomic electronics form a spherically symmetric, gaussian distribution around the nucleus. We can write the electron density for a single atom centered at the origin as

$$\rho_j(r) = Z_j \cdot f_{\sigma_j}(r)$$

where Z_j is the atomic number and the gaussian distribution is

$$f_{\sigma}(r) = \frac{1}{\sigma^3 (2\pi)^{3/2}} \cdot \exp\left[-\frac{1}{2} \left(\frac{r}{\sigma}\right)^2\right]$$

which is normalized in 3-D.

$$\rho_m(\mathbf{r}) = \sum_j \rho_j(|\mathbf{r} - \mathbf{r}_j|) = \sum_j Z_j \cdot f_{\sigma_j}(|\mathbf{r} - \mathbf{r}_j|)$$

The square of the electron density is then

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$$\rho_m^2(\mathbf{r}) = \sum_{j,j'} Z_j \cdot Z_{j'} \cdot f_{\sigma_j}(|\mathbf{r} - \mathbf{r}_j|) \cdot f_{\sigma_{j'}}(|\mathbf{r} - \mathbf{r}_{j'}|)$$

Assuming the atoms are well separated, so that the overlap of the gaussians is negligible, the only contributions occur when $j' = j$. So

$$\rho_m^2(\mathbf{r}) \approx \sum_j Z_j^2 \cdot f_{\sigma_j}^2(|\mathbf{r} - \mathbf{r}_j|)$$

This is equivalent to writing

$$\rho_m^2(\mathbf{r}) \approx \sum_j \rho_j^2(|\mathbf{r} - \mathbf{r}_j|)$$

We note that

$$f_{\sigma}^2(r) = \frac{1}{\sigma^3 (2\pi)^{3/2}} \cdot f_{\sigma/\sqrt{2}}(r)$$

Then

$$\rho_m^2(\mathbf{r}) \approx \sum_j \frac{Z_j^2}{\sigma_j^3 (2\pi)^{3/2}} \cdot f_{\sigma_j/\sqrt{2}}^2(|\mathbf{r} - \mathbf{r}_j|)$$

Now we assume that the atoms are all identical, so $Z_j = Z$ and $\sigma_j = \sigma$. Then

$$\rho_m(\mathbf{r}) = Z \cdot \sum_j f_{\sigma}(|\mathbf{r} - \mathbf{r}_j|)$$

and

$$\rho_m^2(\mathbf{r}) \approx \frac{Z}{\sigma^3 (2\pi)^{3/2}} \cdot \left[Z \cdot \sum_j f_{\sigma/\sqrt{2}}(|\mathbf{r} - \mathbf{r}_j|) \right]$$

Notice that, except for the different gaussian widths, the two functions are proportional:

$$\rho_m^2(\mathbf{r}) \approx \frac{Z}{\sigma^3 (2\pi)^{3/2}} \cdot \rho_m(\mathbf{r})$$

We conclude that, for crystals with atoms spanning only a small range of atomic numbers, and which are well-separated, it is valid to approximate

$$\rho^2(\mathbf{r}) \propto \rho(\mathbf{r})$$

Sayre's equation

We know the electron density can be written as a Fourier series:

$$\rho(\mathbf{r}) = \frac{1}{v} \sum_{\mathbf{H}} F_{\mathbf{H}} \cdot e^{-2\pi i \mathbf{r}_{\mathbf{H}} \cdot \mathbf{r}}$$

The structure factors are

$$F_{\mathbf{H}} = F(\mathbf{r}_{\mathbf{H}}^*) = \sum_j f_j(\mathbf{r}_{\mathbf{H}}^*) \cdot e^{2\pi i \mathbf{r}_{\mathbf{H}}^* \cdot \mathbf{r}_j}$$

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where

$$f_j(\mathbf{r}^*) = T[\rho_j(\mathbf{r})]$$

Likewise,

$$\rho^2(\mathbf{r}) = \frac{1}{v} \sum_{\mathbf{H}} G_{\mathbf{H}} \cdot e^{-2\pi i \mathbf{r}_{\mathbf{H}}^* \cdot \mathbf{r}}$$

With our assumption of well-spaced atoms, the Fourier components are

$$G_{\mathbf{H}} = G(\mathbf{r}_{\mathbf{H}}^*) = \sum_j g_j(\mathbf{r}_{\mathbf{H}}^*) \cdot e^{2\pi i \mathbf{r}_{\mathbf{H}}^* \cdot \mathbf{r}_j}$$

where

$$g_j(\mathbf{r}^*) = T[\rho_j^2(\mathbf{r})]$$

If all atoms are identical, $f_j(\mathbf{r}_{\mathbf{H}}^*) = f(\mathbf{r}_{\mathbf{H}}^*) = f_{\mathbf{H}}$, and $g_j(\mathbf{r}_{\mathbf{H}}^*) = g(\mathbf{r}_{\mathbf{H}}^*) = g_{\mathbf{H}}$. So

$$F_{\mathbf{H}} = f_{\mathbf{H}} \cdot \sum_j e^{2\pi i \mathbf{r}_{\mathbf{H}}^* \cdot \mathbf{r}_j}$$

$$G_{\mathbf{H}} = g_{\mathbf{H}} \cdot \sum_j e^{2\pi i \mathbf{r}_{\mathbf{H}}^* \cdot \mathbf{r}_j}$$

We observe that $F_{\mathbf{H}}/f_{\mathbf{H}} = G_{\mathbf{H}}/g_{\mathbf{H}}$. Defining $\theta_{\mathbf{H}} = f_{\mathbf{H}}/g_{\mathbf{H}}$, we have $F_{\mathbf{H}} = \theta_{\mathbf{H}} G_{\mathbf{H}}$, so

$$F_{\mathbf{H}} = \frac{\theta_{\mathbf{H}}}{v} \sum_{\mathbf{H}'} F_{\mathbf{H}'} \cdot F_{\mathbf{H}-\mathbf{H}'}$$

This is useful for crystals that match our assumptions of having atoms with (nearly) identical atomic numbers, which are well-spaced (minimal overlap).

Example: identical, delta-function atoms

In the limit $\sigma \rightarrow 0$, the gaussians describing the atom shapes become delta functions:

$$\rho_m(\mathbf{r}) = Z \sum_j \delta_j(|\mathbf{r} - \mathbf{r}_j|)$$

Recall that the structure factors are components of the Fourier transform of the electron density.

$$F_m(\mathbf{r}^*) = T[\rho_m(\mathbf{r})]$$

We designate those components by the Miller indices for the reciprocal lattice vectors. In this case:

$$\begin{aligned} F_{\mathbf{H}} &= F(\mathbf{r}_{\mathbf{H}}^*) = \int_{\mathbf{r}} d^3 r \cdot \rho_m(\mathbf{r}) \cdot \exp(2\pi i \mathbf{r}_{\mathbf{H}}^* \cdot \mathbf{r}) \\ &= Z \cdot \sum_j \exp(2\pi i \mathbf{r}_{\mathbf{H}}^* \cdot \mathbf{r}_j) \end{aligned}$$

We can use these to find the Fourier components of the electron density squared:

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$$\begin{aligned}
 G_H &= \frac{1}{v} \sum_{H'} F_{H'} \cdot F_{H-H'} = \frac{Z^2}{v} \cdot \sum_{H'} \sum_{j,j'} \exp(2\pi i \mathbf{r}_{H'}^* \cdot \mathbf{r}_j) \cdot \exp(2\pi i \mathbf{r}_{H-H'}^* \cdot \mathbf{r}_{j'}) \\
 &= \frac{Z^2}{v} \cdot \sum_{H'} \sum_{j,j'} \exp(2\pi i \mathbf{r}_{H'}^* \cdot \mathbf{r}_j) \cdot \exp[2\pi i (\mathbf{r}_j^* - \mathbf{r}_{H'}^*) \cdot \mathbf{r}_{j'}] \\
 G_H &= \frac{Z^2}{v} \cdot \sum_{j,j'} \exp(2\pi i \mathbf{r}_{H'}^* \cdot \mathbf{r}_{j'}) \cdot \sum_{H'} \exp[2\pi i \mathbf{r}_{H'}^* \cdot (\mathbf{r}_j - \mathbf{r}_{j'})]
 \end{aligned}$$

We will define a discrete function representing the sum over H. Because there are an infinite number of RLVs, the sum vanishes if $\mathbf{r}_j - \mathbf{r}_{j'} \neq \mathbf{0}$, and diverges if $\mathbf{r}_j - \mathbf{r}_{j'} = \mathbf{0}$.

$$M_{j,j'} \doteq \sum_{H'} \exp[2\pi i \mathbf{r}_{H'}^* \cdot (\mathbf{r}_j - \mathbf{r}_{j'})] = \begin{cases} \infty, & j = j' \\ 0, & j \neq j' \end{cases}$$

We are only interested in the non-zero Fourier coefficients, so we just need the divergent value:

$$M \doteq M_{0,0}$$

Now the Fourier components of ρ^2 are

$$\begin{aligned}
 G_H &= \frac{Z^2 \cdot M}{v} \cdot \sum_j \exp(2\pi i \mathbf{r}_H^* \cdot \mathbf{r}_j) = \frac{Z \cdot M}{v} \cdot \left[Z \cdot \sum_j \exp(2\pi i \mathbf{r}_H^* \cdot \mathbf{r}_j) \right] \\
 G_H &= \frac{Z \cdot M}{v} \cdot F_H
 \end{aligned}$$

Using the relation between F_H and G_H :

$$\frac{Z \cdot M}{v} \cdot F_H = \frac{1}{v} \sum_{H'} F_{H'} \cdot F_{H-H'}$$

So we can write Sayre's equation for this case:

$$F_H = \frac{1}{Z \cdot M} \sum_{H'} F_{H'} \cdot F_{H-H'}$$

The division by M is a little puzzling, because this is infinite. Unlike a real crystal, the structure factors for this delta-function crystal do not show an overall decrease with scattering vector, and there are infinitely many of them contributing to the sum. We are essentially taking an average over the terms in the sum.

Using Sayre's equation

Let's simplify Sayre's equation

$$F_H = k \cdot \sum_{H'} F_{H'} \cdot F_{H-H'}$$

If we multiply by $F_{-H} = F_H^*$, we have

$$|F_H|^2 = k \cdot \sum_{H'} F_H \cdot F_{H'} \cdot F_{H-H'}$$

This quantity is real and non-negative. Using Friedel's law, we can write

$$|F_H|^2 = k \cdot \sum_{H'} |F_H| \cdot |F_{H'}| \cdot |F_{H-H'}| \cdot \exp[i(-\phi_H + \phi_{H'} + \phi_{H-H'})]$$

If F_H is a strong reflection, and we find two other strong reflections $F_{H'}$ and $F_{H-H'}$, they may dominate the sum, so we can ignore all of the other terms. In this case, we know that

$$-\phi_H + \phi_{H'} + \phi_{H-H'} \approx 0$$

So we can estimate the phase of F_H using

$$\phi_H \approx \phi_{H'} + \phi_{H-H'}$$

Let's consider a centrosymmetric crystal. We always put the inversion center at the origin, so the structure factors are real. We know that $\phi_H = 0, \pi$, where $F_H = |F_H| \cdot e^{i\phi_H}$. Alternatively, we can refer to the sign as $S_H = \pm 1$, so $F_H = S_H \cdot |F_H|$. Then we have

$$S_H \approx S_{H'} \cdot S_{H-H'}$$

This leaves four possible combinations, instead of the eight we would have otherwise:

$$(+) = (+) \cdot (+)$$

$$(+) = (-) \cdot (-)$$

$$(-) = (+) \cdot (-)$$

$$(-) = (-) \cdot (+)$$

Unitary structure factors

We often write the structure factors as

$$F_H = \sum_j f_j \cdot e^{2\pi i r_H^* \cdot r_j}$$

This ignores the fact that the atomic form factors f_j depend on scattering vector r_H^* . Strictly speaking, this only holds for point-like (delta-function) atoms, but is a fair approximation for real atoms within a narrow range of r_H^* . *Unitary* structure factors are defined as

$$E_H = \frac{F_H}{\sigma} = \sum_j v_j \cdot e^{2\pi i r_H^* \cdot r_j}$$

where division is by the sum of form factors $\sigma = \sum_j f_j$, which is equal to F_0 for point-like atoms, so $E_0 = 1$. Consider the quantity

$$E_H + E_{-H} = \sum_j v_j \cdot (e^{2\pi i \bar{H} \cdot X_j} + e^{-2\pi i \bar{H} \cdot X_j}) = 2 \sum_j v_j \cdot \cos(2\pi \bar{H} \cdot X_j)$$

Each term can be factored as follows:

$$E_H + E_{-H} = 2 \sum_j \sqrt{v_j} \cdot [\sqrt{v_j} \cdot \cos(2\pi \bar{H} \cdot X_j)]$$

Cauchy-Schwarz inequality

Now consider two vectors in some abstract Hilbert space:

$$\mathbf{a} = \sum_j a_j \hat{\mathbf{e}}_j \quad \text{and} \quad \mathbf{b} = \sum_j b_j \hat{\mathbf{e}}_j$$

The inner product is the analog of the dot product in this space:

$$\mathbf{a} \cdot \mathbf{b} = \sum_j a_j \cdot b_j = a \cdot b \cdot \cos \theta$$

The inner product of each vector with itself gives the vector's euclidean norm (length) squared:

$$\mathbf{a} \cdot \mathbf{a} = a^2 = \sum_j a_j^2 \quad \text{and} \quad \mathbf{b} \cdot \mathbf{b} = b^2 = \sum_j b_j^2$$

Since $(\mathbf{a} \cdot \mathbf{b})^2 = a^2 \cdot b^2 \cdot \cos^2 \theta$, we have

$$\left(\sum_j a_j \cdot b_j \right)^2 = \left(\sum_j a_j^2 \right) \cdot \left(\sum_j b_j^2 \right) \cdot \cos^2 \theta$$

The angle θ in this abstract space is hard to visualize, but we know $0 \leq \cos^2 \theta \leq 1$, so

$$\left(\sum_j a_j \cdot b_j \right)^2 \leq \left(\sum_j a_j^2 \right) \cdot \left(\sum_j b_j^2 \right)$$

which is called the Cauchy-Schwarz inequality.

Harker-Kasper inequality

Let's identify $a_j = 2\sqrt{v_j}$ and $b_j = \sqrt{v_j} \cdot \cos(2\pi\bar{H}X_j)$. Then

$$\begin{aligned} |E_H + E_{-H}|^2 &\leq \left[\sum_j (2\sqrt{v_j})^2 \right] \cdot \left\{ \sum_{j'} \left[\sqrt{v_{j'}} \cdot \cos(2\pi\bar{H} \cdot X_{j'}) \right]^2 \right\} \\ &\leq 4 \cdot \left(\sum_j v_j \right) \cdot \left[\sum_{j'} v_{j'} \cdot \cos^2(2\pi\bar{H} \cdot X_{j'}) \right] \\ &\leq 4 \cdot \sum_j v_j \cdot \left\{ \frac{1}{2} [1 + \cos(4\pi\bar{H} \cdot X_j)] \right\} \\ &\leq 2 \cdot \left\{ \left(\sum_j v_j \right) + \sum_{j'} v_{j'} \cdot \cos(4\pi\bar{H} \cdot X_{j'}) \right\} \\ |E_H + E_{-H}|^2 &\leq 2 \cdot \left[1 + \sum_j v_j \cdot \cos(4\pi\bar{H} \cdot X_j) \right] \end{aligned}$$

For point-like atoms, the last term is related to E_{2H} , giving

$$|E_H + E_{-H}|^2 \leq 2 + E_{2H} + E_{-2H}$$

or

$$E_{2H} + E_{-2H} \geq |E_H + E_{-H}|^2 - 2$$

Using $E_H = |E_H| \cdot e^{i\phi_H}$, we have

$$E_H + E_{-H} = 2|E_H| \cdot \cos \phi_H \quad \text{and} \quad E_{2H} + E_{-2H} = 2|E_{2H}| \cdot \cos \phi_{2H}$$

so

$$|E_{2H}| \cdot \cos \phi_{2H} \geq 2|E_H|^2 \cdot \cos^2 \phi_H - 1$$

It is easiest to consider centrosymmetric crystals at this point. Because E_H is real, and $E_{-H} = E_H^*$, we know $E_{-H} = E_H$. So

$$E_{2H} \geq 2E_H^2 - 1$$

Instead of phases, we only have to consider signs, i.e., $E_{2H} = S_{2H} \cdot |E_{2H}|$, where $S_{2H} = \pm 1$. Now

$$S_{2H} \cdot |E_{2H}| \geq 2E_H^2 - 1$$

Karle-Hauptman inequalities

Recall that

$$F_H = F(\mathbf{r}_H^*) = T[\rho_m(\mathbf{r})] = \int_{\mathbf{r}} \rho_m(\mathbf{r}) \cdot e^{-2\pi i \mathbf{r}_H^* \cdot \mathbf{r}} \cdot d^3 r$$

Using $\bar{\mathbf{A}}^* \cdot (\mathbf{H} - \mathbf{H}') = \bar{\mathbf{A}}^* \cdot \mathbf{H} - \bar{\mathbf{A}}^* \cdot \mathbf{H}' = \mathbf{r}_H^* - \mathbf{r}_{H'}^*$, we can write

$$F_{H-H'} = \int_{\mathbf{r}} \rho_m(\mathbf{r}) \cdot e^{-2\pi i (\mathbf{r}_H^* - \mathbf{r}_{H'}^*) \cdot \mathbf{r}} \cdot d^3 r$$

Now let's define the quantity

$$\begin{aligned} S &= \int_{\mathbf{r}} \rho_m(\mathbf{r}) \cdot |X(\mathbf{r})|^2 \cdot d^3 r \geq 0 \\ &= \int_{\mathbf{r}} \rho_m(\mathbf{r}) \cdot X^*(\mathbf{r}) \cdot X(\mathbf{r}) \cdot d^3 r \\ &= \int_{\mathbf{r}} \rho_m(\mathbf{r}) \cdot \left(\sum_{H'} X_{H'}^* \cdot e^{2\pi i \mathbf{r}_{H'}^* \cdot \mathbf{r}} \right) \cdot \left(\sum_H X_H \cdot e^{-2\pi i \mathbf{r}_H^* \cdot \mathbf{r}} \right) \cdot d^3 r \\ &= \sum_{H, H'} X_{H'}^* \cdot X_H \int_{\mathbf{r}} \rho_m(\mathbf{r}) \cdot e^{-2\pi i (\mathbf{r}_H^* - \mathbf{r}_{H'}^*) \cdot \mathbf{r}} \cdot d^3 r \\ S &= \sum_{H, H'} X_H^* \cdot X_{H'} \cdot F_{H-H'} = \bar{\mathbf{X}} \cdot \mathbf{F} \cdot \mathbf{X} \end{aligned}$$

We have noted that the above quantity is non-negative, because it involves integral of the product of the electron density (which is non-negative) with the magnitude of a second periodic function that is also non-negative. We can, in principle, evaluate this quantity using infinite matrices:

$$S = \begin{pmatrix} X_{H_1}^* & X_{H_2}^* & \dots \end{pmatrix} \cdot \begin{pmatrix} F_{H_1-H_1} & F_{H_2-H_1} & \dots \\ F_{H_1-H_2} & F_{H_2-H_2} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \cdot \begin{pmatrix} X_{H_1} \\ X_{H_2} \\ \vdots \end{pmatrix} \geq 0$$

However, Karle and Hauptman argued that the product is only assured to be non-negative if $\det(\mathbf{F}) \geq 0$.

Thus, we know that the structure factors of any crystal will satisfy this condition:

$$\begin{vmatrix} F_0 & F_{H_1-H_2}^* & \dots \\ F_{H_1-H_2} & F_0 & \dots \\ \vdots & \vdots & \ddots \end{vmatrix} \geq 0$$

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using that fact that $F_{-H} = F_H^*$. We often only include only a subset of strong reflections in F , and interpret the above in equality to represent a probable situation, that is $\det(F)$ is *probably* not negative.

We can easily write a form of F using unitary structure factors without affecting the inequality. If the crystal is centrosymmetric, then $E_H = E_H^* = E_{-H}$, so the matrix is symmetric. For example:

$$\begin{vmatrix} 1 & E_{H_1} & E_{H_2} \\ E_{H_1} & 1 & E_{H_1-H_2} \\ E_{H_2} & E_{H_1-H_2} & 1 \end{vmatrix} \geq 0$$

Example 1: We include only 0 and one strong reflection H .

$$\begin{vmatrix} 1 & E_H \\ E_H & 1 \end{vmatrix} \geq 0$$

implies $1 - E_H^2 \geq 0$, so $E_H^2 \leq 1$, and $-1 \leq E_H \leq 1$, which is not too surprising.

Example 2: We include only 0 and strong reflections H and $2H$.

$$\begin{vmatrix} 1 & E_H & E_{2H} \\ E_H & 1 & E_H \\ E_{2H} & E_H & 1 \end{vmatrix} \geq 0$$

A few lines of algebra (and the fact that $E_{2H} \leq 1$) show that

$$E_{2H} \geq 2E_H^2 - 1$$

which is the Harker-Kasper inequality.

Example 3: We include only 0 and strong reflections H and H' .

$$\begin{vmatrix} 1 & E_H & E_{H'} \\ E_H & 1 & E_{H'-H} \\ E_{H'} & E_{H'-H} & 1 \end{vmatrix} \geq 0$$

The algebra in this case shows that

$$E_H \cdot E_{H'} \cdot E_{H'-H} \geq \frac{1}{2}(E_H^2 + E_{H'}^2 + E_{H'-H}^2 - 1)$$