

# Commentationes

## Applications of Fourier Transforms in Molecular Orbital Theory

### II. Evaluation of Frenkel Exciton Lattice Sums

John S. Avery

Kemisk Laboratorium IV, H. C. Ørsted Institute, University of Copenhagen

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Fourier transform methods introduced by Harris are applied to the evaluation of Frenkel exciton lattice sums. The slowly-convergent direct lattice sum is converted into a rapidly-convergent reciprocal lattice sum which includes all orders in the multipole expansion. A simple example is discussed, and the calculated exciton energy as a function of wave number is compared with the results of the Ewald method.

*Key words:* Frenkel exciton lattice sums – Fourier transforms in MO theory

#### 1. Introduction

In Frenkel exciton theory [1–12], one is interested in evaluating lattice sums of the form:

$$H_{i \rightarrow j; k \rightarrow l}(\mathbf{q}) = \sum_{\mathbf{x} \neq 0} e^{i\mathbf{q} \cdot \mathbf{x}} \int d^3x \int d^3x' \rho_{i \rightarrow j}^*(\mathbf{x}') \frac{e^2}{|\mathbf{x} - \mathbf{x}'|} \rho_{k \rightarrow l}(\mathbf{x} - \mathbf{X}) \quad (1)$$

In Eq. (1),  $\mathbf{q}$  is the exciton wave number, and the set of vectors  $\{\mathbf{X}\}$  form the direct lattice of a crystal.

$\rho_{i \rightarrow j}$  and  $\rho_{k \rightarrow l}$  are “transition charge densities” defined by the relationships:

$$\begin{aligned} \rho_{i \rightarrow j}^*(\mathbf{x}') &\equiv \varphi_i(\mathbf{x}') \varphi_j^*(\mathbf{x}') \\ \rho_{k \rightarrow l}(\mathbf{x}) &\equiv \varphi_k^*(\mathbf{x}) \varphi_l(\mathbf{x}) \end{aligned} \quad (2)$$

where  $\varphi_i, \varphi_j, \varphi_l$  are molecular orbitals. The usual method for evaluating Frenkel exciton lattice sums of the form (1) is to expand  $1/|\mathbf{x} - \mathbf{x}'|$  in a Taylor series about the points  $\mathbf{x} = \mathbf{X}$  and  $\mathbf{x}' = \mathbf{X}'$ :

$$\frac{1}{|\mathbf{x} - \mathbf{x}'|} = \left\{ 1 + (\mathbf{x} - \mathbf{X}) \cdot \frac{\partial}{\partial \mathbf{X}} + (\mathbf{x}' - \mathbf{X}') \cdot \frac{\partial}{\partial \mathbf{X}'} + \dots \right\} \frac{1}{|\mathbf{X} - \mathbf{X}'|} \quad (3)$$

Substituting (3) into (1) and letting  $X' = 0$ , one obtains as the leading term, the dipole-dipole interaction:

$$H_{i \rightarrow j; k \rightarrow l}(\mathbf{q}) = e^2 \sum_{\mathbf{x} \neq 0} e^{i\mathbf{q} \cdot \mathbf{x}} \left\{ \frac{\mathbf{D}_{i \rightarrow j}^* \cdot \mathbf{D}_{k \rightarrow l}}{|\mathbf{X}|^3} - \frac{3(\mathbf{D}_{i \rightarrow j} \cdot \mathbf{X})(\mathbf{D}_{k \rightarrow l} \cdot \mathbf{X})}{|\mathbf{X}|^5} \right\} \quad (4)$$

where

$$\mathbf{D}_{i \rightarrow j} \equiv \int d^3x \rho_{i \rightarrow j}(\mathbf{x}) \mathbf{x} \quad (5)$$

Dipolar lattice sums of the type shown in Eq. (4) have been studied by Cohen and Keffer [13] using mathematical methods developed by Ewald, Born and Bradburn [14-16]. In this paper, we shall instead evaluate the lattice sum shown in Eq. (1) using the full Coulomb interaction [17-18] rather than the dipole-dipole approximation. To do this, we shall make use of Fourier transform methods similar to those introduced by Harris [19-26].

### 2. Fourier Transform Evaluation of $H_{i \rightarrow j; k \rightarrow l}(\mathbf{q})$

If we introduce the Fourier transform representation of  $1/|\mathbf{x} - \mathbf{x}'|$ :

$$\frac{1}{|\mathbf{x} - \mathbf{x}'|} = \frac{1}{2\pi^2} \int \frac{d^3k}{k^2} e^{i\mathbf{k} \cdot (\mathbf{x} - \mathbf{x}')} \quad (6)$$

then we can rewrite (1) in the form:

$$H_{i \rightarrow j; k \rightarrow l}(\mathbf{q}) = \frac{e^2}{2\pi^2} \sum_{\mathbf{x} \neq 0} e^{i\mathbf{q} \cdot \mathbf{x}} \int \frac{d^3k}{k^2} e^{i\mathbf{k} \cdot \mathbf{x}} \rho_{i \rightarrow j}^{*T}(-\mathbf{k}) \rho_{k \rightarrow l}^T(\mathbf{k}) \quad (7)$$

where

$$\rho_{i \rightarrow j}^T(\mathbf{k}) \equiv \int d^3x e^{i\mathbf{k} \cdot \mathbf{x}} \rho_{i \rightarrow j}(\mathbf{x}) \quad (8)$$

is the Fourier transform of the transition charge density  $\rho_{i \rightarrow j}$ . General methods for evaluating Fourier transforms of this type have been discussed by Monkhorst and Harris [32], by Graovac, Monkhorst and Zivkovic [33], and by Harris [26]. We now make use of the relationship [26]:

$$\sum_{\mathbf{x}} e^{i(\mathbf{k} + \mathbf{q}) \cdot \mathbf{x}} = \frac{(2\pi)^3}{v} \sum_{\mathbf{K}} \delta(\mathbf{k} + \mathbf{q} + \mathbf{K}) \quad (9)$$

In Eq. (9),  $v$  is the volume of a unit cell, while the set of vectors  $\{\mathbf{K}\}$  forms a lattice reciprocal to the direct lattice  $\{\mathbf{X}\}$ . Substituting (9) into (7), we obtain the result:

$$H_{i \rightarrow j; k \rightarrow l}(\mathbf{q}) = \frac{4\pi e^2}{v} \sum_{\mathbf{K}} \frac{\rho_{i \rightarrow j}^{*T}(\mathbf{K} + \mathbf{q}) \rho_{k \rightarrow l}^T(-\mathbf{K} - \mathbf{q})}{|\mathbf{K} + \mathbf{q}|^2} - \Delta H \quad (10)$$

where  $\Delta H$  is the term corresponding to  $\mathbf{X} = 0$ :

$$\Delta H \equiv \frac{e^2}{2\pi^2} \int \frac{d^3k}{k^2} \rho_{i \rightarrow j}^{*T}(-\mathbf{k}) \rho_{k \rightarrow l}^T(\mathbf{k}) \quad (11)$$

The reciprocal lattice sum (10) converges rapidly because  $\rho_{i \rightarrow j}^{*T}(-\mathbf{k})$  and  $\rho_{k \rightarrow l}^T(\mathbf{k})$  fall off very rapidly with  $k$ , as illustrated in the example given below.

### 3. Periodicity

Notice that the expression for  $H_{i \rightarrow j; k \rightarrow l}(\mathbf{q})$  given in (10) has the periodicity of the reciprocal lattice, since

$$\begin{aligned} H_{i \rightarrow j; k \rightarrow l}(\mathbf{q} + \mathbf{K}') + \Delta H &= \frac{4\pi e^2}{v} \sum_{\mathbf{K}} \frac{\rho_{i \rightarrow j}^{*T}(\mathbf{K} + \mathbf{K}' + \mathbf{q}) \rho_{k \rightarrow l}^T(-\mathbf{K} - \mathbf{K}' - \mathbf{q})}{|\mathbf{K} + \mathbf{K}' + \mathbf{q}|^2} \\ &= \frac{4\pi e^2}{v} \sum_{\mathbf{K}'' = \mathbf{K} + \mathbf{K}'} \frac{\rho_{i \rightarrow j}^{*T}(\mathbf{K}'' + \mathbf{q}) \rho_{k \rightarrow l}^T(-\mathbf{K}'' - \mathbf{q})}{|\mathbf{K}'' + \mathbf{q}|^2} = H_{i \rightarrow j; k \rightarrow l}(\mathbf{q}) + \Delta H \end{aligned} \quad (12)$$

### 4. Behavior near $\mathbf{q} = 0$

We would like to investigate the behavior of  $H_{i \rightarrow j; k \rightarrow l}(\mathbf{q})$  in the neighbourhood of the point  $\mathbf{q} = 0$ . The leading term in the series is then the term corresponding to  $\mathbf{K} = 0$ . For very small values of  $\mathbf{q}$ , the remainder of the series, (i.e. the sum of the terms for which  $\mathbf{K} \neq 0$ ), is approximately independent of  $\mathbf{q}$ . Thus we can write:

$$H_{i \rightarrow j; k \rightarrow l}(\mathbf{q}) \underset{\mathbf{q} \rightarrow 0}{\cong} \frac{4\pi e^2}{v} \frac{\rho_{i \rightarrow j}^{*T}(\mathbf{q}) \rho_{k \rightarrow l}^T(-\mathbf{q})}{|\mathbf{q}|^2} + \frac{4\pi e^2}{v} \sum_{\mathbf{K} \neq 0} \frac{\rho_{i \rightarrow j}^{*T}(\mathbf{K}) \rho_{k \rightarrow l}^T(-\mathbf{K})}{|\mathbf{K}|^2} - \Delta H \quad (13)$$

In the neighborhood of  $\mathbf{q} = 0$ , we have:

$$\begin{aligned} \lim_{\mathbf{q} \rightarrow 0} \rho_{i \rightarrow j}^T(\mathbf{q}) &= \lim_{\mathbf{q} \rightarrow 0} \int d^3x e^{i\mathbf{q} \cdot \mathbf{x}} \rho_{i \rightarrow j}(\mathbf{x}) \\ &= i\mathbf{q} \cdot \int d^3x x \rho_{i \rightarrow j}(\mathbf{x}) \mathbf{x} \equiv i\mathbf{q} \cdot \mathbf{D}_{i \rightarrow j} \end{aligned} \quad (14)$$

Thus, in the neighborhood of  $\mathbf{q} = 0$ , we have the approximate relation:

$$\begin{aligned} H_{i \rightarrow j; k \rightarrow l}(\mathbf{q}) \underset{\mathbf{q} \rightarrow 0}{\cong} \frac{4\pi e^2}{v} \frac{(\mathbf{q} \cdot \mathbf{D}_{i \rightarrow j}^*)(\mathbf{q} \cdot \mathbf{D}_{k \rightarrow l})}{q^2} + \frac{4\pi e^2}{v} \sum_{\mathbf{K} \neq 0} \frac{\rho_{i \rightarrow j}^{*T}(\mathbf{K}) \rho_{k \rightarrow l}^T(-\mathbf{K})}{|\mathbf{K}|^2} \\ - \frac{e^2}{2\pi^2} \int \frac{d^3k}{k^2} \rho_{i \rightarrow j}^{*T}(\mathbf{k}) \rho_{k \rightarrow l}^T(-\mathbf{k}) \end{aligned} \quad (15)$$

### 5. A Lattice of Hydrogen Molecules

In order to illustrate the use of Eq. (15), let us apply it to a simple idealized example: a lattice of hydrogen molecules arranged as shown in Fig. (1). The ground state molecular orbital and the first excited state orbital of a single hydrogen molecule are given respectively by:

$$\begin{aligned} \varphi_1 &= \frac{1}{\sqrt{2\pi a_0^3}} (e^{-|\mathbf{x}-\mathbf{l}/a_0|} + e^{-|\mathbf{x}+\mathbf{l}/a_0|}) \\ \varphi_2 &= \frac{1}{\sqrt{2\pi a_0^3}} (e^{-|\mathbf{x}-\mathbf{l}/a_0|} - e^{-|\mathbf{x}+\mathbf{l}/a_0|}) \end{aligned} \quad (16)$$

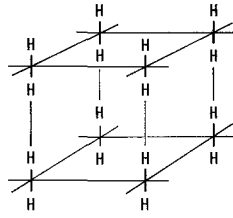


Fig. 1. A cubic lattice of hydrogen molecules is chosen as an idealized example to illustrate Eq. (10)

where  $a_0$  is the Bohr radius and  $2l$  is the  $H-H$  separation. Thus the transition density is given by:

$$\rho_{1 \rightarrow 2} \equiv \varphi_1^* \varphi_2 = \frac{1}{2\pi a_0^3} (e^{-2|x-l|/a_0} - e^{-2|x+l|/a_0}) \quad (17)$$

and the Fourier transform of the transition density is:

$$\rho_{1 \rightarrow 2}^T(\mathbf{k}) = \frac{i\zeta^4 \sin(\mathbf{k} \cdot \mathbf{l})}{\{k^2 + \zeta^2\}^2} \quad \zeta = \frac{2}{a_0} \quad (18)$$

while the transition dipole moment becomes:

$$\mathbf{D}_{1 \rightarrow 2} = \int d^3x \rho_{1 \rightarrow 2}(\mathbf{x}) \mathbf{x} = \mathbf{l} \quad (19)$$

If we substitute (18) into (10) and perform the sum in reciprocal space for a cubic lattice, we obtain the exciton energy as a function of the wave number  $\mathbf{q}$  in the band corresponding to the transition  $1 \rightarrow 2$ . The surfaces corresponding to constant energy in this band are shown in Fig. (2). The point  $\mathbf{q} = 0$  is singular, as are other points displaced from  $\mathbf{q} = 0$  by reciprocal lattice vectors. Many contours of constant energy, corresponding to different energies, converge on the point  $\mathbf{q} = 0$ . Thus the value of the lattice sum at  $\mathbf{q} = 0$  depends on the direction from which the point is approached. In order to examine the region near the point  $\mathbf{q} = 0$ , we can substitute (18) and (19) into (15). This yields

$$H_{1 \rightarrow 2, 1 \rightarrow 2}(\mathbf{q}) \underset{\mathbf{q} \rightarrow 0}{\cong} \frac{4\pi e^2 (\mathbf{q} \cdot \mathbf{l})(\mathbf{q} \cdot \mathbf{l})}{v q^2} + \frac{4\pi e^2 \zeta^8}{v} \sum_{\mathbf{K} \neq 0} \frac{\sin^2(\mathbf{K} \cdot \mathbf{l})}{|\mathbf{K}|^2 \{|\mathbf{K}|^2 + \zeta^2\}^4} - \Delta H \quad (20)$$

The integral

$$\Delta H = \frac{e^2 \zeta^8}{2\pi^2} \int \frac{d^3k \sin^2(\mathbf{k} \cdot \mathbf{l})}{k^2 \{k^2 + \zeta^2\}^4} \quad (21)$$

can be rewritten in the form:

$$\Delta H = \frac{e^2 \zeta^8}{4\pi^2} \{I(0) - \frac{1}{2}I(2l) - \frac{1}{2}I(-2l)\} \quad (22)$$

where

$$I(R) \equiv 4\pi \int_0^\infty \frac{dk j_0(kR)}{\{k^2 + \zeta^2\}^4} \quad (23)$$

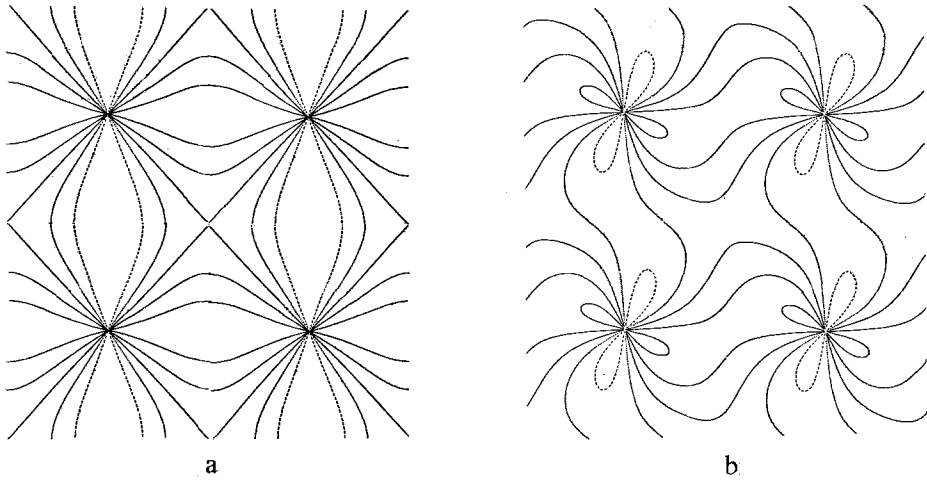


Fig. 2. These figures show exciton energy as a function of wave number for the transition  $1 \Rightarrow 2$ , (Eq. (16)). Curves of constant energy, calculated from Eq. (10) are shown in reciprocal space. The curves fulfil two requirements: Firstly, near the point  $q=0$  the exciton energy is given by Eq. (27), and secondly, the exciton energy as a function of wave number has the periodicity of the reciprocal lattice. In Fig. (2a), the transition dipole moment points along one of the crystal lattice vectors, as shown in Fig. (1). In Fig. (2b), the molecular axis and the transition dipole moment are rotated through an angle of  $30^\circ$  in one of the crystal planes

In (23),  $j_0$  is a spherical Bessel function of order zero. Evaluating  $I(R)$  by contour integration, we obtain:

$$I(R) = \frac{(4\pi)^2}{3(2\zeta)^7(\zeta R)} [48 - e^{-\zeta R} \{48 + 33\zeta R + 9(\zeta R)^2 + (\zeta R)^3\}] \tag{24}$$

With  $2l = 1.4a_0$  and  $\zeta = 2/a_0$ , substitution of (25) into (22) yields

$$\Delta H = 0.060739534 \frac{e^2}{a_0} \tag{25}$$

The reciprocal lattice sum in (20) converges rapidly because of the high power of  $K$  in the denominator. When this sum is evaluated numerically and combined with the value of the integral, we obtain the approximate result:

$$\frac{4\pi e^2 \zeta^2}{v} \sum_{\mathbf{K} \neq 0} \frac{\sin^2(\mathbf{K} \cdot \mathbf{l})}{|\mathbf{K}|^2 \{|\mathbf{K}|^2 + \zeta^2\}^4} - \frac{e^2 \zeta^8}{2\pi^2} \int \frac{d^3k \sin^2(\mathbf{k} \cdot \mathbf{l})}{k^2 \{k^2 + \zeta^2\}^4} \cong \frac{4\pi e^2 l^2}{3v} \tag{26}$$

Thus, in the neighborhood of  $q=0$ , we find the approximate relationship:

$$H_{1 \rightarrow 2, 1 \rightarrow 2}(\mathbf{q}) \cong \frac{4\pi e^2}{v} \left\{ \frac{(\mathbf{q} \cdot \mathbf{l})(\mathbf{q} \cdot \mathbf{l})}{q^2} - \frac{l^2}{3} \right\} \tag{27}$$

### 6. Comparison with the Results of Cohen and Keffer

Cohen and Keffer [13], using the methods of Ewald, Born and Bradburn [14-16], obtain the following expression for the lattice sum of the dipole-dipole

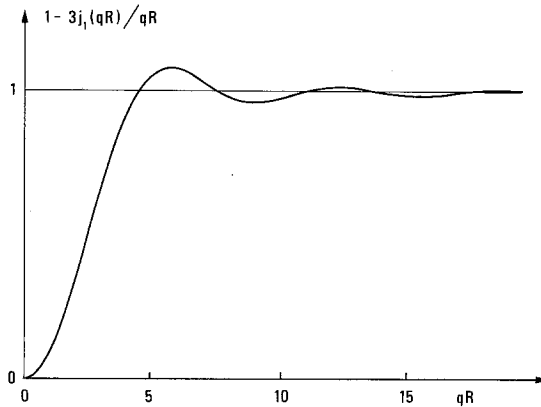


Fig. 3. According to the Cohen-Keffer formula, Eq. (28), the contribution of the dipole-dipole interaction vanishes at  $q=0$  for finite crystals. This is because the factor  $1 - 3j_1(qR)/qR$  vanishes when  $qR=0$ . Thus, for finite crystals, the point  $q=0$  becomes a saddle point rather than an essential singularity

interaction (Eq. (4)) in the neighborhood of the point  $q=0$ :

$$H_{i \rightarrow j; k \rightarrow l}(\mathbf{q}) \underset{q \rightarrow 0}{\cong} \frac{4\pi e^2}{v} \left\{ \frac{(\mathbf{q} \cdot \mathbf{D}_{i \rightarrow j})(\mathbf{q} \cdot \mathbf{D}_{k \rightarrow l})}{q^2} - \frac{1}{3} \mathbf{D}_{i \rightarrow j} \cdot \mathbf{D}_{k \rightarrow l} \right\} \times \left\{ 1 - \frac{3j_1(qR)}{qR} \right\} \quad (28)$$

Here the lattice sum is evaluated for a finite spherical crystal of radius  $R$ , and  $j_1$  is a spherical Bessel function of order 1. When  $R \rightarrow \infty$  and  $q \rightarrow 0$  simultaneously, the value of  $q=0$  obtained from Cohen and Keffer's formula is indeterminate. However, when  $R$  is held at a finite value and  $q \rightarrow 0$ , the value at  $q=0$  is unambiguously zero, since

$$1 - \frac{3j_1(qR)}{qR} \underset{qR \rightarrow 0}{\Rightarrow} 0 \quad (29)$$

According to Cohen and Keffer's formula, when  $R$  is finite, rapid oscillations in  $H_{i \rightarrow j; k \rightarrow l}(\mathbf{q})$  should occur in the neighborhood of  $q=0$  because of the factor  $1 - 3j_1(qR)/qR$  illustrated in Fig. (3). When  $R$  is infinite and  $q$  is small but finite,

$$1 - \frac{3j_1(qR)}{qR} \underset{qR \rightarrow \infty}{\Rightarrow} 1 \quad (30)$$

and (28) reduces to

$$H_{i \rightarrow j; k \rightarrow l}(\mathbf{q}) \underset{\substack{R \rightarrow \infty \\ q \ll 1/a_0}}{\Rightarrow} \frac{4\pi e^2}{v} \left\{ \frac{(\mathbf{q} \cdot \mathbf{D}_{i \rightarrow j})(\mathbf{q} \cdot \mathbf{D}_{k \rightarrow l})}{q^2} - \frac{\mathbf{D}_{i \rightarrow j} \cdot \mathbf{D}_{k \rightarrow l}}{3} \right\} \quad (31)$$

which should be compared with Eqs. (19 and (27)). Notice that the Fourier transform evaluation of the lattice sum differs from the Ewald method by including all of the high multipoles as well as the dipole-dipole contribution. (For a discussion of the high multipoles, see Silbey, Jortner and Rice, Ref. [17]). However, in the particular example which we have been discussing, the dipole-dipole contribution

is very large in comparison to the contribution of higher multipoles, and therefore we get an approximate agreement between the two methods even though one includes the higher multipoles and the other does not.

## 7. Discussion

Fourier transform methods can be seen to be very useful in the evaluation of Frenkel exciton lattice sums. These methods can also be used to evaluate Madelung sums, as has been discussed by Dahl [27] and Harris [26]. A Madelung sum is a sum of the form shown in Eq. (1), evaluated at the point  $\mathbf{q}=0$ , with the transition densities replaced by the total charge density. In this context, the Cohen-Keffler formula (26) might be used to discuss the contribution of the dipole-dipole term at  $\mathbf{q}=0$ .

The formalism outlined above can also be adapted to the evaluation of lattice sums when relativistic effects and retardation are included [28–31]. In that case, one can introduce the Fourier transform representation of the Green's function of the operator  $\nabla^2 + \kappa^2$ :

$$(\nabla^2 + \kappa^2)G(\mathbf{x}, \mathbf{x}') = -4\pi\delta(\mathbf{x} - \mathbf{x}') \quad (32)$$

$$G(\mathbf{x}, \mathbf{x}') = \frac{1}{2\pi^2} \int \frac{d^3k e^{ik \cdot (\mathbf{x} - \mathbf{x}')}}{k^2 - \kappa^2}$$

instead of Eq. (6). I hope to discuss these problems in detail in another paper.

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Dr. J. S. Avery  
Kemisk Laboratorium IV  
H. C. Ørsted Institute  
University of Copenhagen  
Universitetsparken 5  
Copenhagen, Denmark