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# Fourier Representation Methods for Møller-Plesset Perturbation Theory in One-Dimensionally Periodic Systems

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**Abstract.** Ab initio studies of one-dimensionally periodic systems are advantageously carried out by methods that employ Fourier representations and the Ewald method for accelerating the lattice sums. This communication describes the first investigation in which these techniques have been applied at the Møller-Plesset level of perturbation theory, MBPT(2). Second-order corrections to the restricted Hartree-Fock energy and energy bands are reported for H<sub>2</sub>, Be, and LiH chains, and these results are compared to direct-space extended-system and oligomer computations. The methods described herein exhibit improved convergence relative to the other methods to which they are compared.

**Keywords:** electronic structure of polymers, Fourier methods, Ewald method, Møller-Plesset theory, one-dimensionally periodic systems, band structure of polymers

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## INTRODUCTION

Interpretation and prediction of the structural and electronic properties of polymers are often based on model systems with periodicity in one dimension. The currently most popular method for purely theoretical calculations of the electronic structure of extended systems is density functional theory (DFT). However, DFT includes electron correlation approximately and because most current functionals are not always adequate, a number of properties (band gap, ionization potentials, intermolecular interactions, ...) are not properly described. This situation has been reviewed in a number of studies [1-4]. Accordingly, methodologies based on the Hartree-Fock theory and beyond retain their interest and obtaining suitable methods leading towards reliable and efficient computer codes should be continued.

Direct-space approaches to ab initio electronic-structure calculations on periodic systems are known to involve lattice sums that converge only slowly, and inappropriate lattice sum truncations can lead to significant numerical errors [5]. This problem has been addressed using multipole expansions and similar techniques [6]; the convergence characteristics of the lattice sums (for coulombic, and exchange contributions) are now well known, as are those arising in correlation calculations at the Møller-Plesset [now often designated MBPT(2)] level.

The most satisfactory way to overcome lattice-sum convergence problems is to use the now well-known Ewald procedure [7], which partitions each lattice sum into two subsums, of which the less rapidly convergent is then transformed to a more convergent form using Fourier representations and the Poisson summation theorem. These techniques were applied by Harris and Monkhorst in 1970 [8] to periodic systems described in an atomic basis, and developed specifically by I. Flamant and the present authors [9] for application, using Gaussian-type orbitals, to systems periodic in one dimension. This approach, which has not previously been applied to the computation of correlation energy in a periodic system, is the subject of the present communication.

The systems investigated here include H<sub>2</sub>, Be and LiH chains, and the properties studied include total energies, band energies, and band gaps. Our values of these quantities are compared with those from direct-space extended-system methods and with oligomer computations. The results confirm the validity of our methods and illustrate the improvement in convergence relative to direct-space computations.

## WAVEFUNCTIONS AND ENERGY FORMULAS

All our calculations were carried out using restricted Hartree-Fock (RHF) orbitals  $\phi_\mu(k, \mathbf{r})$  built from basis functions of Bloch type, of generic form

$$\phi_\mu(k, \mathbf{r}) = \sum_{m=-\infty}^{\infty} \chi_\mu(k, \mathbf{r} - ma_0\hat{\mathbf{z}})e^{2\pi imk}, \quad (1)$$

where  $\hat{\mathbf{z}}$  is a unit vector in the  $z$  direction, and the system has periodicity in that direction, with cell dimension  $a_0$ . The variable  $k$ , in the range  $(-\frac{1}{2}, \frac{1}{2})$ , defines a point in the unit-scaled Brillouin zone. The  $\chi_\mu(k, \mathbf{r})$  are  $k$ -dependent linear combinations of Gaussian-type orbitals (GTO's) centered in a reference cell; the coefficients were determined by solving the RHF equations on grids of equally spaced  $k$  values. For the systems studied in the present work, only spherically symmetric GTO's were used. Further information regarding the RHF computations is in Ref. [9], and detailed formulas for the GTO integrals were given in the dissertation of I. Flamant [10].

We now introduce a compact notation in which  $\langle k_1k_3|k_2k_4\rangle_{\mu\nu,\sigma\tau} = \langle \phi_\mu(k_1, \mathbf{r}_1)\phi_\nu(k_3, \mathbf{r}_2)|r_{12}^{-1}|\phi_\sigma(k_2, \mathbf{r}_1)\phi_\tau(k_4, \mathbf{r}_2)\rangle$ , where  $k_3$  is the value of  $k_2 + k_4 - k_1$  after a lattice vector translation if needed to bring it back into the first Brillouin zone. Then, for a closed-shell system in which  $i, j$  and  $a, b$  respectively denote occupied and unoccupied RHF Bloch orbitals, the following formulas [2,3,11,12] have been derived for  $E^{(2)}$ , the MBPT(2) correction to the energy per unit cell, and  $\varepsilon_p^{(2)}(k)$ , the corresponding correction to the band energy of band  $p$  (where  $p$  may be either occupied or unoccupied):

$$E^{(2)} = \int_{-\frac{1}{2}}^{\frac{1}{2}} dk_1 \int_{-\frac{1}{2}}^{\frac{1}{2}} dk_2 \int_{-\frac{1}{2}}^{\frac{1}{2}} dk_4 \sum_{ijab} Q_{ij,ab}(k_1; k_2, k_4); \quad (2)$$

$$\varepsilon_p^{(2)}(k) = \int_{-\frac{1}{2}}^{\frac{1}{2}} dk_2 \int_{-\frac{1}{2}}^{\frac{1}{2}} dk_4 \left[ \sum_{jab} Q_{pj,ab}(k; k_2, k_4) + \sum_{ijb} Q_{pb,ij}(k; k_2, k_4) \right]. \quad (3)$$

The function  $Q$  has the form

$$Q_{\mu\nu,\sigma\tau}(k_1; k_2, k_4) = \frac{|\langle k_1k_3|k_2k_4\rangle_{\mu\nu,\sigma\tau}|^2 + |\langle k_1k_3|k_4k_2\rangle_{\mu\nu,\tau\sigma}|^2 - \Re e [\langle k_1k_3|k_2k_4\rangle_{\mu\nu,\sigma\tau}^* \langle k_1k_3|k_4k_2\rangle_{\mu\nu,\tau\sigma}]}{\varepsilon_\mu(k_1) + \varepsilon_\nu(k_3) - \varepsilon_\sigma(k_2) - \varepsilon_\tau(k_4)}. \quad (4)$$

The key quantities in the above formulas for energetic quantities are the integrals  $\langle k_1k_3|k_2k_4\rangle_{\mu\nu,\sigma\tau}$ , which are easily expanded into lattice sums of atomic one-and two-electron integrals. We note that the integrals needed for MBPT(2) computations are of the same sort as those entering RHF computations, and all can be evaluated using methods described in our previous work [9,10].

## FOURIER METHOD

The reason there is a need for Fourier representation methods is that the lattice sums exhibit severe convergence problems, even in the present relatively simple case of one-dimensional periodicity. The problem is not severe for the one-electron integral lattice sums, which exhibit exponential convergence, but even then the convergence rate can for certain ranges of the basis parameters be improved using Fourier representations. However, the two-electron integral lattice sums include contributions that, even if properly grouped, converge (irrespective of the parameter values) only as  $1/r^2$ , making it important to use the Ewald convergence acceleration process.

The essence of the Ewald process is to write  $1/r$  as its integral representation

$$\frac{1}{r} = \left( \frac{2}{\pi^{1/2}} \right) \int_0^\infty e^{-r^2 t^2} dt, \quad (5)$$

after which the integration is broken into the two ranges  $t = (0, \tau)$  and  $t = (\tau, \infty)$ . Lattice sums (essentially on  $r$ ) will converge exponentially for the range  $t = (\tau, \infty)$ , and exponential convergence for the range  $t = (0, \tau)$  is achieved by using the Poisson summation formula, which replaces a lattice sum of a function  $f$  by that of its Fourier transform

$f^T$ . In the language of condensed-matter physics, this amounts to converting a direct-space lattice sum (in the present context only convergent as  $1/r^2$ ) into an exponentially convergent direct-space sum plus an (also exponentially convergent) reciprocal-space sum.

When this program is carried out for GTO lattice sums, the direct-space contribution to the two-electron integral sum can be reduced to a sum of quantities of the type occurring in all GTO integral evaluations, while the reciprocal-space contribution takes a form involving the incomplete Bessel function  $K_0(x,y)$ , defined as

$$K_0(x,y) = \int_1^\infty \exp\left(-xt - \frac{y}{t}\right) dt. \quad (6)$$

$K_0$  occurs in a variety of physical applications; methods for its evaluation in ranges needed for electronic structure problems have been discussed in Refs. [13] and [14]; we also note a recent paper containing a full review of computational methods for this function [15].

## COMPUTATIONS

Our computer program for carrying out the calculations reported here is named FTCHAIN. It is designed to use contracted STO-nG atomic basis functions for the description of one-dimensionally periodic systems. For H<sub>2</sub> and LiH, we used standard H and Li STO-3G basis sets (*s* functions only); for Be, we used the DSGF-3-21G basis described in Ref. [16]. For all these systems we carried out RHF calculations with the lattice sums extended as necessary to reach a convergence limit of  $10^{-6}$  in the elements of the density matrix.

The  $k$  integrations in the formulas of Eqs. (2) and (3) were carried out numerically, using equal numbers of  $k$  points for each integral. One of the three integrals of Eq. (2) was evaluated using concatenated nine-point (eight subinterval) Newton-Cotes formulas; the remaining integrations, and both integrations in Eq. (3), were performed using a two-dimensional simplex method [17]. Calculations were performed for equally spaced grids of  $k$  consisting of 8, 16, and 32 points. The RHF calculations were well converged for the 32-point grid; the MBPT(2) computations were still incompletely converged at this grid and results were therefore reported as a function of grid size.

For comparison with the results of the present study, some periodic-system computations were carried out using the PLH direct-space program [18]. We also made a number of oligomer calculations, using GAUSSIAN-03 [19]. We examined both linear and circular (cyclic) oligomers, and computed energetic quantities as increments when one additional monomer was added to the oligomer in a suitably extrapolated limit.

## RESULTS AND DISCUSSION

We examined (1) a linear chain of H<sub>2</sub> molecules, at H–H bond length 1.42 bohr, with one molecule per unit cell of dimension 4.00 bohr; (2) a linear LiH chain with one molecule per unit cell of dimension 6.48 bohr, the atoms equally spaced at 3.24 bohr; and (3) linear chains of Be atoms, one per unit cell of dimensions 3.00, 2.75, and 2.50 Å.

For H<sub>2</sub> and LiH, all the methods, oligomer, direct-space (PLH), and the present research (FTCHAIN), gave results in good agreement for the RHF energies. The oligomer and FTCHAIN MBPT(2) energy corrections  $E^{(2)}$  were also in good agreement; there was a very small discrepancy relative to the PLH values of  $E^{(2)}$ , probably attributable to a less complete convergence of the lattice sums. Looking now at one-electron properties (band energies and band gaps), we see that, for LiH, the discrepancy widens. Typical data are shown in Table 1, which displays calculations of the HOMO-LUMO band gap. These data are indicative of the fact, previously commented upon by Sun and Bartlett [2], that a direct-lattice summation to an extent just sufficient for the energy will not be adequate for the one-electron properties. Because the methods of the present study lead to exponential convergence (as opposed to the  $1/r^2$  convergence encountered in an exclusively direct-lattice approach), the FTCHAIN results are the more accurate. Note that the bulk of the discrepancy cannot be attributed to a lack of convergence with respect to the  $k$  grid; the difference between the results using 16 and 32  $k$ -points is far smaller than the discrepancy in  $E^{(2)}$  for LiH.

**TABLE 1.** HOMO-LUMO energy gap (hartrees) for the H<sub>2</sub> and LiH chains described in the text and for the Be chain at cell dimension 2.5 Å. PLH = direct space computation, FTCHAIN = this research.

		H <sub>2</sub>		LiH		Be
		FTCHAIN	PLH	FTCHAIN	PLH	FTCHAIN
RHF		0.80090	0.80090	0.38296	0.38296	0.10559
MBPT(2)	8 <i>k</i> -points	0.78983		0.30863		0.06010
	16 <i>k</i> -points	0.79014		0.30899		0.04922
	21 <i>k</i> -points		0.79018		0.30612	
	32 <i>k</i> -points	0.79017		0.30903		0.04848

The results for Be also indicate advantages to the present approach. At cell dimensions 2.75 Å and 3.00 Å, the quality of both the PLH and FTCHAIN results is comparable to that observed for LiH. But at the smaller cell dimension 2.50 Å, the direct-space lattice-sum convergence problems become so acute that it is even difficult to obtain RHF convergence. The column for Be in Table 1 indicates that the methods of the present study enable RHF and MBPT(2) study of the Be chain without substantial difficulty.

Further detail on the work reported here can be found elsewhere [20].

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