A Wannier function based \textit{ab initio} Hartree-Fock approach extended to polymers: applications to the LiH chain and \textit{trans}-polyacetylene

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Abstract

A recently proposed \textit{ab initio} Hartree-Fock approach aimed at directly obtaining the Wannier functions of a crystalline insulator is applied to polymers. The systems considered are the LiH chain and \textit{trans}-polyacetylene. In addition to being the first application of our approach to one-dimensional systems, this work also demonstrates its applicability to covalent systems. Both minimal as well as extended basis sets were employed in the present study and excellent agreement was obtained with the Bloch orbital based approaches. Cohesive energies, optimized lattice parameters and the band structure are presented. Localization characteristics of the Wannier functions are also discussed.
I. INTRODUCTION

Polymers represent a class of one-dimensional infinite crystalline systems where \textit{ab initio} Hartree-Fock (HF) methods are well developed\cite{1,2,3,4,5,6,7,8,9}. In addition, several groups have gone beyond the HF level and have included the influence of electron correlations as well\cite{10,11,12,13,14}. Owing to the reduced dimensionality, generally, the computational effort involved in an \textit{ab initio} study of a polymer is considerably less than that in the case of a corresponding three-dimensional (3D) crystal. It is possible, therefore, to perform high-quality \textit{ab initio} calculations for polymers which are generally not yet feasible for 3D solids.

Barring a few exceptions involving studies using Wannier-type orbitals\cite{15,16,17,18,19,20,21,22}, the method of choice to study the electronic structure of polymers is based on the use of Bloch orbitals. Even where Wannier functions (WF) were used, they were obtained by \textit{a posteriori} localization of Bloch orbitals. Recently, we have proposed an approach to the electronic structure of periodic insulators which is formulated entirely in terms of Wannier functions\cite{23,24,25,26,27,28,29}, without using Bloch orbitals in any of the intermediate steps. The theory underlying this approach, which deals with the direct determination of the Hartree-Fock Wannier orbitals of a crystalline insulator, is treated in detail in refs.\cite{27,28}. The equivalence of the Wannier-function-based approach to the Bloch-orbital-based approach at the HF level was demonstrated for quantities as diverse as total energy, X-ray structure factors, Compton profiles, band structure, bulk modulus etc. of some 3D ionic insulators such as LiH\cite{27}, LiF\cite{28}, LiCl\cite{28}, NaCl\cite{29}, Li\textsubscript{2}O\cite{27} and Na\textsubscript{2}O\cite{28}. However, owing to the highly localized nature of electronic states in ionic compounds, they are naturally more amenable to a Wannier-function-based approach than covalent systems. Therefore, by presenting HF calculations for trans-polyacetylene, the aim of the present work is not only to demonstrate the applicability of our approach to periodic systems of reduced dimensionality, but also the ease with which the present approach can be applied to study covalent systems. In addition to polyacetylene, we also present calculations on a model ionic polymer, namely, an infinite LiH chain. Since for ionic systems the long-range electrostatic contributions are very important, an accurate treatment of the Coulomb lattice sums becomes of crucial importance here; by comparing our results with those of other authors, we can gauge the accuracy of the treatment of long-range Coulomb interaction in our work. In all the calculations both minimal and extended basis sets were used. For LiH, only total energies at the optimized lattice constants were computed. For polyacetylene, in addition, we present the detailed band structure and cohesive energy. Our main motivation behind adopting a Wannier function based approach is, of course, its possible use in an \textit{ab initio} treatment of electron correlation effects in infinite periodic systems. This aspect of our work will be explored in the next paper in this series. In addition, the Wannier functions also offer the possibility of an \textit{ab initio} determination of parameters involved in various model Hamiltonians formulated in terms of localized orbitals such as the Hückel model\cite{30}, the Hubbard model\cite{31} and the Pariser-Parr-Pople (PPP) model\cite{32}. We will also investigate these possibilities in a future publication.

The remainder of the paper is organized as follows. In Section II, we briefly sketch the theory with particular emphasis on the treatment of the Coulomb lattice sums which differs from our Ewald-summation based approach adopted for the 3D crystals. In Section III, we present the results of our calculations, while Section IV contains our conclusions.
II. THEORY

A. Hartree-Fock Equations

For the sake of completeness, in this section we briefly review the underlying theory in an intuitive manner. Rigorous derivations, along with details pertaining to the computer implementation, can be found in our previous papers. To solve the Hartree-Fock problem of an infinite periodic system in the Wannier representation (as against the traditional Bloch representation) we adopt a “divide and conquer” strategy. In this approach, we partition the infinite system into a reference cell called the central cluster ($C$), and its environment ($E$) consisting of the rest of the infinite number of unit cells. Thus, we can envision $C$ as a cluster embedded in the field of the rest of the infinite solid. Since the translational symmetry requires that the orbitals localized in two different unit cells be identical to each other (except for their location), it clearly suffices for us to know the orbitals of the central cluster only, whereas the orbitals of all other cells can be generated from them by simple translation operations. If we restrict the use of the Greek indices $\alpha$, $\beta$ and $\gamma$ etc. to denote the (occupied) Wannier orbitals of the reference cell, and accordingly choose the set $\{|\alpha\rangle; \alpha = 1, n_c\}$ to represent the Wannier functions of the $2n_c$ electrons localized in $C$, then the condition of translational symmetry can be expressed as

$$|\alpha(R_i)\rangle = T(R_i)|\alpha(0)\rangle,$$

where $|\alpha(0)\rangle$ represents a Wannier orbital localized in the reference unit cell assumed to be located at the origin while $|\alpha(R_i)\rangle$ is the corresponding orbital of the $i$-th unit cell located at lattice vector $R_i$, and the corresponding translation is induced by the operator $T(R_i)$. This immediately suggests an iterative self-consistent-field (SCF) procedure. We can start the calculations with a reasonable starting guess for the orbitals of $C$, and consequently those of $E$. These orbitals, in turn, can be used to set up the embedded-cluster Hamiltonian for the electrons of $C$, which, upon diagonalization, leads to a new set of orbitals. This procedure can be iterated until self-consistency is achieved indicated by a converged value of the total energy per cell. Clearly, the above mentioned SCF procedure is applicable to any independent-particle effective Hamiltonian such as the Kohn-Sham or the Hartree-Fock Hamiltonian. However, in what follows, we will focus exclusively on the ab initio restricted Hartree-Fock (RHF) implementation of the embedded-cluster approach outlined above. In our previous work we showed that one can obtain a set of RHF Wannier functions of the $2n_c$ electrons localized in $C$ by solving the equations:

$$(T + U + \sum_\beta (2J_\beta - K_\beta) + \sum_{k \in \mathbb{N}} \sum_{\gamma} \lambda_{k\gamma} |\gamma(R_k)\rangle \langle \gamma(R_k)|)|\alpha\rangle = \epsilon_\alpha |\alpha\rangle,$$  

where $T$ represents the kinetic-energy operator, $U$ represents the interaction of the electrons of $C$ with the nuclei of the whole of the polymer while $J_\beta$, $K_\beta$ defined as

$$J_\beta |\alpha\rangle = \sum_j \langle \beta(R_j)| \frac{1}{r_{ij}} |\beta(R_j)\rangle |\alpha\rangle,$$

$$K_\beta |\alpha\rangle = \sum_j \langle \beta(R_j)| \sum_{r_{ij}} |\alpha\rangle |\beta(R_j)\rangle$$

respectively incorporate the Coulomb and exchange interactions of the electrons of $C$ with those of the infinite system. The first three terms of Eq. (2) constitute the canonical Hartree-Fock operator, while the last term is a projection operator which makes the orbitals localized
in $\mathcal{C}$ orthogonal to those localized in the unit cells in the immediate neighborhood of $\mathcal{C}$ by means of infinitely high shift parameters $\lambda^k \gamma$’s. These neighborhood unit cells, whose origins are labeled by lattice vectors $\mathbf{R}_k$, are collectively referred to as $\mathcal{N}$. The projection operators along with the shift parameters play the role of a localizing potential in the Fock matrix, and once self-consistency has been achieved, the occupied eigenvectors of Eq.(2) are localized in $\mathcal{C}$, and are orthogonal to the orbitals of $\mathcal{N}$—thus making them Wannier functions. As far as the orthogonality of the orbitals of $\mathcal{C}$ to those contained in unit cells beyond $\mathcal{N}$ is concerned, it should be automatic for systems with a band gap once $\mathcal{N}$ has been chosen to be large enough. In what follows we shall specify the size of $\mathcal{N}$ by specifying the number $N$ which implies the number of nearest neighbors that are included in $\mathcal{N}$. For example, $N = 3$ shall imply that $\mathcal{N}$ contains up to third-nearest neighbors of $\mathcal{C}$, and so on. The influence of the choice of $N$ on the results of the calculations will also be studied in section III.

We have computer-implemented the formalism outlined above within a linear combination of atomic orbitals (LCAO) scheme, utilizing Gaussian-lobe-type basis functions. We proceed by expanding the orbitals localized in the reference cell as

$$|\alpha\rangle = \sum_p \sum_{\mathbf{R}_j \in \mathcal{C} + \mathcal{N}} C_{p\mathbf{R}_j,\alpha} |p(\mathbf{R}_j)\rangle,$$

where $\mathcal{C}$ has been used to denote the reference cell, $\mathbf{R}_j$ represents the location of the $j$th unit cell (located in $\mathcal{C}$ or $\mathcal{N}$) and $|p(\mathbf{R}_j)\rangle$ represents a lobe-type basis function centered in the $j$th unit cell. In order to account for the orthogonalization tails of the reference cell Wannier orbitals, it is necessary to include the basis functions centered in $\mathcal{N}$ as well. The main aspect which makes the problem of the infinite solid different from the problem of a molecule that one usually encounters in quantum chemistry, is the presence of infinite lattice sums in the terms $U$, $J$ and $K$ of Eq.(2). Of these, the exchange interaction depicted by $K$ is fairly short-range for insulators, and converges rapidly. However, the terms $U$ and $J$ involve long-range Coulomb interactions and are individually divergent. Therefore, they need special consideration. In our work on 3D insulators published earlier, we resorted to the Ewald-summation technique in order to evaluate these contributions. But, for the case of one-dimensional systems considered here, we use a completely real-space summation approach to be discussed in the next subsection.

To obtain the band structure we adopt the approach outlined in our previous work. This essentially consists of first Fourier transforming the converged real-space Fock matrix (cf. Eq.(2)) to get its k-space representation, and then rediagonalizing it to obtain the band energies and eigenvectors.

B. Treatment of the Coulomb Series

The matrix elements of electron-nucleus interaction that one needs to construct the LCAO version of Eq.(2) for the case of a polymer are

$$U_{pq}(t_{pq}) = - \sum_{j=-M}^{M} \sum_{A} \langle p(t_{pq}) | \frac{Z_A}{|\mathbf{r} - \mathbf{R}_j - \mathbf{r}_A|} |q(0)\rangle,$$

where $|p(t_{pq})\rangle$ and $|q(0)\rangle$ denote two basis functions separated by an arbitrary vector of the lattice $t_{pq}$. $\mathbf{R}_j$ denotes the location of a unit cell, $Z_A$ represents the nuclear charge of the
\( A \)-th atom of the unit cell, \( \mathbf{r}_A \) represents its fractional coordinates, and the summation over \( A \) naturally runs over all the atoms in the unit cell. Of course, for an infinite polymer \( M \to \infty \). Similarly, to describe the Coulombic part of the electron-electron repulsion, we need matrix elements of the form

\[
J_{pq;rs}(\mathbf{t}_{pq}, \mathbf{t}_{rs}) = \sum_{j=-M}^{M} \langle p(\mathbf{t}_{pq}) | r_{pq} + \mathbf{R}_j | 1 \rangle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | q(0) \rangle \langle s(0) | r_{rs} + \mathbf{R}_j | 1 \rangle ,
\]

which, by means of a coordinate transformation, can be brought into a form very similar to that of Eq. (5)

\[
J_{pq;rs}(\mathbf{t}_{pq}, \mathbf{t}_{rs}) = \sum_{j=-M}^{M} \langle p(\mathbf{t}_{pq}) | r_{pq} | 1 \rangle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{R}_j|} | q(0) \rangle \langle s(0) | r_{rs} + \mathbf{R}_j | 1 \rangle .
\]

Although the individually infinite series involved in Eqs. (5) and (7) are divergent, they can be forced to converge by means of the Ewald-summation method\(^{35,36}\). However, if one uses one and the same, sufficiently large value of \( M \) to directly evaluate the matrix elements of Eqs. (5) and (7), the divergences inherent in the two terms will cancel each other owing to the opposite signs when combined together to form the corresponding Fock matrix element. The total energy per unit cell will also be convergent if one uses the same value of \( M \) to evaluate the contribution of the nucleus-nucleus interaction energy as well. Besides the finite lattice sums over the unit cell index \( j \) in the equations above, we have not included any other long-range corrections such as ones based upon multipole expansions\(^6\). The real-space approach outlined above is similar in spirit to the one used by Dovesi in his Bloch orbital based study of polyacetylene\(^\text{10}\). Most of the other authors also adopt the real-space based summation of the Coulomb series to perform \textit{ab initio} studies on polymers\(^1\text{–}14\). However, these schemes differ in various details related to the cutoff used in the truncation of the series. The convergence properties of the total energy per unit cell and, to some extent its final value, are frequently dependent on the scheme adopted. For an excellent account of different cutoff schemes in practice, and their convergence properties, we refer the reader to a recent article by Teramae\(^\text{14}\).

In the present scheme we calculate only the set of integrals indicated by Eqs. (5) and (6) and generate all the integrals needed from this set by using translational invariance. However, strictly speaking, the translationally invariant form of these equations is valid only in the limit \( M \to \infty \). Since all the calculations presented in this work are restricted to finite values of \( M \), the use of translational invariance embodied in Eqs. (5) and (6) is an approximation. Therefore, it is important to study carefully the convergence of the total energy per unit cell as a function of \( M \) and we will present our findings in Sec. III.

### III. CALCULATIONS AND RESULTS

In this section we present the results of calculations performed on both the model polymer LiH and the "real" polymer \textit{trans}-polyacetylene. To check the accuracy of our approach, we also performed the same calculations with the CRYSTAL program\(^{37}\) and will present those results as well. Since our approach does not include the long-range corrections to
the Coulomb interaction, while the CRYSTAL program does include them via the Ewald summation, we believe that this comparison is quite instructive. Wherever possible, we will also compare our results to those of other authors.

A. LiH

Perhaps because of its simplicity, the LiH chain has been studied by several authors prior to this work. The reason behind our study of this system is twofold. Firstly, being an ionic polymer, the long-range Coulomb interactions are very important for the LiH chain. Since our approach does not rely on an infinite sum of this effect, comparison of our results with those of the CRYSTAL program will help us to judge the quality of our treatment of the Coulomb series. Secondly, as mentioned previously, our program uses lobe functions to approximate the $p$ and higher angular momentum cartesian basis functions. Since most of the other authors use true cartesian basis functions, comparison between our results and those of other programs such as CRYSTAL can only be approximate when such basis functions are involved. However, the LiH chain can be described reasonably well using only $s$-type basis functions, a case for which the lobe- and the cartesian-type Gaussian basis functions are trivially equivalent. Therefore, a comparison of our results for the LiH chain involving only $s$-type Gaussian basis functions with those of other authors, will be a further test of the correctness of our approach.

Karpfen and Delhalle et al. concluded that for an infinite LiH chain, the equilibrium geometry corresponds to the case where Li and H atoms are equidistant from each other. We also adopted a similar geometry, with the reference cell having H at $(0, 0, 0)$ and Li at $(a/2, 0, 0)$, where $a$ is the lattice constant of the chain. The chain was assumed to be oriented along the $x$ axis.

To study the LiH chain with a (sub)-minimal basis set, we adopted the STO-4G basis set optimized by Dovesi et al. for their study of the bulk LiH. Thus, there are two basis functions per unit cell, with one basis function each on Li and H sites. With this basis set we obtained an equilibrium lattice constant of 6.653 atomic units. The results of our calculations at the equilibrium lattice constant, and its comparison with those of the CRYSTAL program, are presented in the table I. To the best of our knowledge, the STO-4G basis has not been used by any other author to study the LiH chain, so that for this case our comparison is restricted only to the CRYSTAL results. For the extended basis set calculations we used the contraction coefficients and the exponents reported by Huzinaga, both for Li and H. The Li basis set was of the type $(8s)/[5s]$ while the H basis set was of $(4s)/[3s]$ type with, in total, eight basis functions per unit cell. This basis set was also used by Delhalle et al. in their study of the LiH infinite chain, employing a multipole-expansion-oriented approach for the Coulomb series. They obtained an equilibrium lattice constant of 6.478 a.u., which is the value that we have also used to perform our computations presented in table II. In the same table, our results are compared with those of Delhalle et al. and those obtained using the CRYSTAL program. In every calculation involving either our program or CRYSTAL, all the one- and two-electron integrals whose absolute value was below $10^{-7}$ a.u. were discarded.

From tables I and II one can easily understand the convergence pattern of our results as far as its dependence on the size of the orthogonality region $N$, and the number of neighbors
in the Coulomb series $M$, is concerned. A quick glance at both the tables reveals that it is not sufficient to orthogonalize the Wannier orbitals of the reference cell $C$ only to those in its nearest neighbor cells ($N = 1$). As is clear, the lack of sufficient orthogonality for those cases leads to energies lower than the true energies. However, if we orthogonalize the Wannier orbitals of $C$ to, at least, those in the second-nearest-neighbor cells ($N = 2$), we attain convergence in total energy per unit cell. This fact is obvious by noticing that the energies obtained with the orthogonality requirement restricted to the second-nearest neighbors ($N = 2$) agree at the micro-Hartree level with those obtained when the orthogonality requirement was extended to the third- ($N = 3$) and the fourth-nearest neighbors ($N = 4$), respectively. This rather fast convergence with respect to $N$ can be understood intuitively if one considers the fact that the LiH chain is a large-band-gap insulator. This, in turn, points to the well-localized character of the valence electrons residing predominantly on the $\text{H}^-$ Wannier functions. With well-localized valence electrons, one should not expect them to have sizeable overlaps with the electrons localized in the far-away unit cells.

Now we examine the convergence of the results with respect to the number of neighbors $M$ included in the Coulomb series. For the reasons mentioned above, we will only consider those of our results which correspond to $N = 2$ or higher. Even a cursory inspection of tables I and II reveals that, as expected, this convergence, is much slower as compared to the one with respect to $N$. This can also be intuitively understood as a consequence of the long-range character of the Coulomb interactions in an ionic system like the LiH chain. Indeed, we find for the case of the minimal basis set that our results are 1 microHartree off the CRYSTAL results. This small disagreement could also be due to some numerical error in either of the codes. For the case of extended basis set we have exact microHartree-level agreement with the results of Delhalle et al.\cite{6} and CRYSTAL\cite{37}, once well-above 200 nearest-neighbors have been included in the Coulomb series. However, for evaluating energy differences in quantum-chemical calculations, it is often sufficient to have results accurate up to 1 milliHartree. As is clear from both the tables, this level of accuracy is achieved with about 40 neighbors included in the Coulomb series. Thus the fact remains that in absolute terms the Coulomb series converges quite slowly; however, for the purpose of a calculation with reasonable accuracy, the computational effort involved in a direct scheme as outlined in Sec. [TB] is not too prohibitive.

### B. Trans-polyacetylene

The isomer trans-polyacetylene(t-PA) has been the subject of numerous studies, both at the Hartree-Fock\cite{4,7,8,9,10,13,14} and at correlated levels\cite{9,16,18,19,21,23}. It has an alternant structure as shown in Fig. [10], with the length of the double bond ($r_2$) being shorter than that of the single bond ($r_1$). The difference in the corresponding bond lengths $\Delta r = r_1 - r_2$ is called the bond alternation. If the two bond lengths were equal, i.e., a zero bond alternation, the unit cell of t-PA will consist of a single CH unit giving it a metallic character with a half-filled $\pi$ band. However, in reality, because of nonzero bond alternation, t-PA has a dimerized unit cell consisting of a $C_2H_2$ unit which naturally leads to insulating behavior. The dimerization is widely believed to be a consequence of Peierls distortion which follows from the coupling of the phonons to electrons on the Fermi surface\cite{41}. The phenomenon of nonexistence of one-dimensional metals due to Peierls distortion—sometimes also referred
to as Peierls dimerization—has come to be known as the Peierls theorem.

In this work we have used the lobe representations of both the minimal STO-3G basis set as well as the extended 6-31G basis set, to optimize the geometry and to obtain the cohesive energies at the Hartree-Fock level. We have used the 6-31G basis set in two versions. Since the use of d-type functions in a lobe representation is computationally very expensive, we have dropped polarization functions on the carbon atoms during our study of the convergence pattern of the Coulomb series with the extended basis set, although polarization functions on the hydrogen atoms were retained. The polarization function on hydrogen consisted of a single p-type exponent of 0.75 a.u. From now on, we refer to this restricted form of the 6-31G basis set with a [3s,2p] basis set on carbon and a [2s,1p] set on hydrogen as the 6-31G-1 basis set. For the geometry optimization and band structure calculations, we augmented the carbon basis by one d-type exponent of 0.55 a.u. and refer to the basis set by its conventional name of 6-31G**. For the sake of comparison, we also performed the same set of calculations with the CRystal program. As in the case of LiH, in both our and CRystal calculations all the one- and two-electron integrals with magnitude less than $1.0 \times 10^{-7}$ a.u. were neglected. In the present calculation, the C-H bond length was assumed to be fixed at the experimental value of 1.09 Å and the reference unit cell was assumed to be a dimerized primitive cell consisting of a C$_2$H$_2$ unit, also shown in Fig. 1. For optimizing the geometry, the bond lengths $r_1$, $r_2$, and the bond angle $\alpha$ between the two C-C bonds were allowed to vary.

To study t-PA at the HF level the STO-3G basis sets have been used earlier by Kertész et al., Suhai, Karpfen et al., Dovesi and recently by Teramae and Suhai. Teramae and Suhai in addition to other lattice parameters also optimized the C-H bond length which was found to be different from the value 1.09 Å used in the present work (as well as by other authors mentioned above). Therefore, we cannot directly compare our results to those of Teramae and Suhai. Of the other authors, only Karpfen et al. and Dovesi performed the geometry optimization. The optimized values for $r_1$, $r_2$ and the bond angle $\alpha$ were obtained to be respectively 1.477 Å, 1.327 Å and 124.2° by Karpfen et al. and 1.486 Å, 1.329 Å and 124.4° by Dovesi. The optimized values of 1.489 Å, 1.326 Å and 124.1° obtained by us in the present work clearly are in good agreement with the previous results.

With the extended 6-31G-1 basis set, the optimized values of $r_1$, $r_2$ and $\alpha$ obtained with our approach were 1.452 Å, 1.340 Å and 124.4°. When we performed the geometry optimization with the same basis set using the CRystal program we obtained 1.458 Å, 1.336 Å and 124.5° for these quantities. When we used the 6-31G** basis set for the same task, the optimized values with our program were 1.457 Å, 1.336 Å and 124.2°, and with the CRystal code we determined them to be 1.464 Å, 1.333 Å and 124.2°. Clearly, for both types of extended basis sets, i.e., with and without polarization functions on the carbon atoms, there is excellent agreement between our optimized geometries and those obtained using the CRystal program.

The convergence pattern of the total energy per unit cell at the optimized geometries mentioned above, as a function of the parameters $M$ and $N$ is displayed in table I for the STO-3G set and in table II for the 6-31G-1 basis set. Contrary to the case of the LiH chain, we were not able to achieve convergence if the orthogonality region of the Wannier functions was smaller than the third-nearest neighbors ($N = 3$). This observation can be understood on the physical grounds that the Wannier functions of a covalent system like t-PA are much...
more delocalized as compared to an ionic system such as the LiH chain. Therefore, their orthogonalization tails extend much more into the neighborhood than those of the Wannier functions of LiH. Although a micro-Hartree level convergence in total energy is achieved only after including at least six nearest-neighbor cells in the orthogonality region, the difference in total energy between the \(N = 3\) and \(N = 6\) cases is only \(\approx 24\) micro Hartrees. Thus the convergence in the total energy with respect to \(N\) is quite rapid.

Similarly, for t-PA the convergence of the total energy per unit cell with respect to the number of nearest neighbors \((M)\) included in the Coulomb series turns out to be slower than for the LiH chain. As is clear from tables [I] and [V], to achieve a milliHartree convergence in the results, one needs to have at least \(M = 75\), while the microHartree convergence is not achieved even after including 500 nearest neighboring cells. With the extended 6-31G-1 basis set we did not achieve any convergence for the cases with \(M = 10\) and \(M = 20\). This behavior is to be contrasted with the case of the LiH chain (tables [I] and [V]) where \(M = 20\) sufficed for a milliHartree level of convergence and about \(M = 200\) brought the results to within 1 microHartree of the converged results. Moreover, in most of the prevalent real-space based approaches to the Coulomb series one observes much faster convergence of the total energy, with reasonable results obtainable even for \(M = 3\) case. Comparatively speaking, the slow convergence of the Coulomb series observed by us appears contradictory. However, the reason behind this can be readily understood if one recognizes the primitive nature of the truncation criteria embodied in Eqs. (5) and (7). This cutoff scheme clearly pays little regard to the charge balance in the unit cell. In addition, it uses translational invariance when, in reality, it is strictly valid only in the limit \(M \to \infty\). Since charge distributions for t-PA are much more delocalized than LiH, any charge imbalance should lead to slower convergence in the former case. This is consistent with our observations. In such a case, would also expect the error due to charge imbalance to diminish with increasing value of \(M\), again consistent with our observations. However, one could accelerate the convergence of the Coulomb series in a computationally inexpensive manner either by adopting an Ewald-summation based approach or by using a multipole expansion based approach. Anyway, for crystalline systems typically results accurate up to milliHartree level are sufficient, and that level of convergence is achieved by using \(M = 75\) which is computationally not too expensive. The comparison of our total energy per unit cell with that obtained using the CRYSTAL program employing the identical geometry is excellent to within a few fractions of a milliHartree. We observed the same level of (dis)agreement with the CRYSTAL results in our previous studies on 3D solids, where we had used the Ewald summation approach to treat the Coulomb series. This gives us confidence that the small disagreements in the total energy per unit cell with respect to the CRYSTAL results are largely due to our use of lobe functions to approximate the cartesian-type Gaussian basis functions used in the CRYSTAL program. Therefore, we believe, that the treatment of the Coulomb series outlined in the present work, although slowly convergent, is conceptually on sound foundations.

We also evaluated the band structure of t-PA, at the most recently reported experimental geometry with \(r_1 = 1.45\) Å, \(r_2 = 1.36\) Å and the lattice constant of 2.455 Å which corresponds to a bond angle \(\alpha = 121.7^\circ\), using the 6-31G** basis set. For these calculations the choice of orthogonality parameter was \(N = 3\) and the Coulomb-series parameter was \(M = 100\). The four highest occupied bands, along with the five lowest conduction bands are plotted in Fig. 2. The same figure also plots the corresponding bands obtained using the
CRYSTAL program employing the same basis set and geometry. The absolute values of the band energies naturally differed somewhat owing to the different treatment of the Coulomb series in the two approaches. Therefore we shifted all the CRYSTAL band energies so that the tops of the valence bands obtained from the two approaches coincided. Clearly, the band structures obtained from the two approaches are in excellent agreement for the occupied bands and for the lowest three conduction bands. The value of the direct band gap (at $k = \frac{\pi}{a}$ point) 0.2356 a.u. (6.41 eV) obtained with our approach is in good agreement with the corresponding CRYSTAL value of 0.2339 a.u. (6.37 eV). For the fourth and the fifth conduction bands we see some small deviations. For the higher conduction bands not plotted in Fig. 2 the deviations are even more significant. However, this behavior is to be expected when one uses lobe functions because, even for molecular systems, unoccupied energy levels generally differ significantly from each other when the same calculation is performed with lobe- and the cartesian-type functions. We saw a similar trend in our earlier work on the band structure of the NaCl crystal. The experimental value of the direct gap is widely believed to be $\approx 2$ eV. Therefore, as is generally the case with HF bands, the band gap of t-PA is overestimated by a large amount, pointing to the importance of the electron correlation effects. The influence of electron correlations on the band structure of t-PA has been studied by Suhai, Liegener and by Sun et al. within Bloch orbital based approaches. Förner et al. have recently included the electron-correlation effects in the band structure using a Wannier-function-based coupled-cluster approach. All the prior studies indicate that once the electron correlations are accounted for, one observes a dramatic reduction in the band gap.

Our results for ground-state properties with the STO-3G basis set are summarized in table V. This table also presents results of other authors who performed calculations using the same basis set. Noteworthy entries in the table are the results of recent calculations by Teramae which were performed using different cutoff schemes for the treatment of the Coulomb series. The details of these cutoff schemes can be obtained in the above-mentioned paper or in the original papers cited therein. The differences in the results with the same basis set but with different cutoff schemes clearly testify to the fact that the treatment of the Coulomb series is a delicate matter which deserves utmost caution. Our own view is that unambiguous results will only be obtained when the Coulomb series is treated in the Ewald limit as is done, e.g. in the CRYSTAL program, or by saturating the Coulomb series to a very large number of unit cells which can be done inexpensively, e.g. by using the multipole expansion techniques of Delhalle et al. In our opinion, these schemes should be treated as standard, and the rest of the prevalent schemes should be judged against them.

Our final results obtained with the extended 6-31G** basis set are presented in table VI which also compares them to the calculations performed by us—employing the same basis set—with the CRYSTAL program. The table also presents the results of Suhai and of Yu et al. which were all performed with basis sets of similar quality as those used by us. To evaluate the cohesive energies corresponding to our calculation, we used Hartree-Fock reference energies for carbon and hydrogen of -37.677838 a.u. and -0.498233 a.u., respectively. These energies were obtained by performing atomic HF calculations employing the same 6-31G basis set as used in the polymer calculations. It is apparent from the table that the results for cohesive energies obtained by different authors, employing different methods and basis sets, are in good agreement. To the best of our knowledge, no experimental data on
the cohesive energy of t-PA are available. However, it is well-known that the HF method systematically underestimates the cohesive energy and, therefore, one expects electron correlations to contribute significantly to the true cohesive energy of t-PA. The experimental geometry of t-PA is available from at least three papers \cite{43,45,46} which disagree from each other somewhat. However, we will use the most recent results of Kahlert et al. \cite{43} as the reference.

Compared to experiment the HF calculations appear to overestimate the single-bond length $r_1$ and bond alternation $\Delta r$ by about 0.01 Å and 0.05 Å respectively, while the double-bond length $r_2$ is underestimated by at least 0.02 Å. The bond-angle, which is a measure of the lattice constant, is also overestimated at the HF level. Therefore, the most significant deviation at the HF level is in the bond alternation. Since the Peierls theorem, which predicts a nonzero bond alternation, is an exact result only in the absence of electron correlations, it is of theoretical interest to study the influence of electron correlations on the phenomenon of Peierls dimerization. The fact that the inclusion of electron correlations improves the agreement with the experiment on all the geometry parameters including bond alternation has been confirmed by König et al. \cite{20} using a “local-ansatz” based approach, by Suhai \cite{17} using a Bloch-orbital-based MBPT approach, and by Yu et al. \cite{25} using an incremental scheme based local-correlation approach \cite{49} applied to finite clusters simulating t-PA.

Finally a pictorial view of the Wannier function corresponding to the $\pi$ bond of the unit cell, evaluated at the experimental geometry, is provided in Fig. 3. The figure corresponds to the contour plot of the charge density associated with the corresponding Wannier function in the $xy$ plane with $z = 0.25$ atomic units. From the contour plots the localized nature of the $\pi$ electrons, as well as their participation in a covalent bond between the two carbon atoms of the unit cell, is obvious.

**IV. CONCLUSIONS AND FUTURE DIRECTIONS**

In conclusion, an *ab initio* Wannier-function-based Hartree-Fock approach developed originally to treat infinite 3D crystalline systems has been extended to deal with polymers. The main difference as compared to the case of 3D systems has been an entirely real-space based treatment of the Coulomb series which has been demonstrated to be applicable both to ionic and covalent systems. We observed slow convergence of the Coulomb series with respect to the lattice sums, but this problem can be rectified in the future by adopting either an Ewald-summation-based, or a multipole-expansion-based approach to the Coulomb series.

The main focus of this work was, of course, a detailed Hartree-Fock study of trans-polyacetylene which involved the use of an extended basis set including polarization-type functions. Various quantities such as the total energy per unit cell, the cohesive energy, optimized geometry parameters and the band structure were found to be in excellent agreement with those found from equivalent calculations performed using the Bloch-orbital-based approach. In this manner we have demonstrated the applicability of our approach to covalent systems where Wannier functions are less well localized as compared to the ionic systems studied earlier by us. One possible use of the present Wannier function based approach can be in the theoretical determination of various parameters involved in model Hamiltonians such as the Hückel Hamiltonian, the PPP and Hubbard models. For the particular case of $\pi$-electron systems such as trans-polyacetylene for the description of which the PPP Hamiltonian is frequently used, one can, after some numerical work, obtain a Hartree-Fock
level estimate of the parameters involved. Such an estimate can subsequently be refined by performing renormalization group procedures. We will pursue this line of research in a separate publication. The Wannier-function based approach can also be used to obtain insights into the various possible mechanisms, such as soliton formation\textsuperscript{33}, supposed to be behind the Peierls distortion of \emph{trans}-polyacetylene. This can be done by introducing the corresponding structural defect in a finite region around the reference cell, keeping the rest of the polymer frozen at the level of the Hartree-Fock solution of the perfect polymer.

The discrepancy between our Hartree-Fock results for \emph{trans}-polyacetylene and the experimental ones was found to be most noteworthy for the bond alternation and the band structure. These differences point to the importance of electron-correlation effects. In a future publication, we will include these within a local-correlation approach to study their effect on ground- and excited-state properties. This way, it will be possible, in particular, to study the influence of electron correlations on the Peierls dimerization within an entirely real-space formalism in an \textit{ab initio} manner, which so far was usually restricted to model Hamiltonians\textsuperscript{31}. 

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FIGURES

FIG. 1. Structure of trans-polyacetylene as considered in the present work. Bonds included in the reference cell $C$ in the calculations are enclosed in the dashed box.

FIG. 2. Band structure of t-PA obtained using our approach (solid lines) compared to that obtained using the CRYSTAL program (dashed lines). The experimental geometry[13] and a 6-31G** basis set was used in both cases. Values of $k$ (horizontal axis) are expressed in units of $\frac{2\pi}{a}$. The two sets of bands are essentially identical except for the top two conduction bands which are somewhat different.

FIG. 3. Contour plots of the charge density of the $\pi$-type valence Wannier function of the reference cell. Contours are plotted in the $xy$ plane with $z = 0.25$ a.u. ($x$ is the axis of the polymer). The magnitude of the contours is on a natural logarithmic scale. The two carbon atoms of the unit cell are located at the positions $(-1.11, 0.64, 0.0)$ a.u. and $(1.11, -0.64, 0.0)$ a.u. respectively. Clearly the dominant contours are surrounding the two carbon atoms of the reference cell indicating a covalent bond between them. Weaker contours due to the orthogonalization tails of the Wannier function extend up to nearest-neighbor carbon atoms and beyond. The rapidly decaying strength of the contours testifies to the localized nature of the Wannier function.
TABLE I. Total energies per unit cell obtained in the present work, as a function of the number of nearest-neighbor unit cells included in the Coulomb series, \((M)\), and those included in the orthogonality region \(\mathcal{N}\) \((\mathcal{N})\). For the sake of comparison, results of equivalent calculations performed with the CRYS TAL\(^{37}\) program, are also reported. The STO-4G minimal basis set of Dovesi et al.\(^{38}\) was used in all the calculations. All the results are in atomic units, and refer to the optimized lattice constant of 6.653 a.u., with equidistant Li and H atoms.

| M    | 1       | 2       | 3       | 4       | CRYS TAL\(^{37}\) |
|------|---------|---------|---------|---------|-------------------|
| 10   | -7.997974 | -7.997898 | -7.997898 | -7.997898 |                   |
| 20   | -7.998249 | -7.998173 | -7.998173 | -7.998173 |                   |
| 30   | -7.998302 | -7.998227 | -7.998227 | -7.998227 |                   |
| 40   | -7.998322 | -7.998246 | -7.998246 | -7.998246 |                   |
| 50   | -7.998330 | -7.998255 | -7.998255 | -7.998255 |                   |
| 100  | -7.998343 | -7.998267 | -7.998267 | -7.998267 |                   |
| 200  | -7.998346 | -7.998270 | -7.998270 | -7.998270 |                   |
| 500  | -7.998346 | -7.998271 | -7.998271 | -7.998271 |                   |
| 1000 | -7.998347 | -7.998271 | -7.998271 | -7.998271 | -7.998272         |
TABLE II. Total energies per unit cell obtained in the present work, as a function of the number of nearest-neighbor unit cells included in the Coulomb series, \( (M) \), and those included in the orthogonality region \( N(N) \). For the sake of comparison, results of other authors are also reported. Extended Huzinaga basis sets\[^3\] were used for Li and H in all the calculations. An optimized lattice constant of 6.478 a.u. was used along with the equidistant Li and H nuclei. All the results are in atomic units.

| M     | N | This Work        | Other Works          |
|-------|---|------------------|----------------------|
| 10    | 1 | -8.035526        | -8.035447            |
|       | 2 | -8.035447        | -8.035447            |
|       | 3 | -8.035447        | -8.035447            |
|       | 4 | -8.035447        | -8.035447            |
| 20    | 1 | -8.035779        | -8.035701            |
|       | 2 | -8.035701        | -8.035701            |
|       | 3 | -8.035701        | -8.035701            |
|       | 4 | -8.035701        | -8.035701            |
| 30    | 1 | -8.035829        | -8.035750            |
|       | 2 | -8.035750        | -8.035750            |
|       | 3 | -8.035750        | -8.035750            |
|       | 4 | -8.035750        | -8.035750            |
| 40    | 1 | -8.035846        | -8.035768            |
|       | 2 | -8.035768        | -8.035768            |
|       | 3 | -8.035768        | -8.035768            |
|       | 4 | -8.035768        | -8.035768            |
| 50    | 1 | -8.035855        | -8.035776            |
|       | 2 | -8.035776        | -8.035776            |
|       | 3 | -8.035776        | -8.035776            |
|       | 4 | -8.035776        | -8.035776            |
| 100   | 1 | -8.035866        | -8.035788            |
|       | 2 | -8.035788        | -8.035788            |
|       | 3 | -8.035788        | -8.035788            |
|       | 4 | -8.035788        | -8.035788            |
| 200   | 1 | -8.035869        | -8.035790            |
|       | 2 | -8.035790        | -8.035790            |
|       | 3 | -8.035790        | -8.035790            |
|       | 4 | -8.035790        | -8.035790            |
| 500   | 1 | -8.035869        | -8.035791            |
|       | 2 | -8.035791        | -8.035791            |
|       | 3 | -8.035791        | -8.035791            |
|       | 4 | -8.035791        | -8.035791            |
| 1000  | 1 | -8.035869        | -8.035791            |
|       | 2 | -8.035791        | -8.035791            |
|       | 3 | -8.035791        | -8.035791            |
|       | 4 | -8.035791        | -8.035791            |

^a^ ref.\[^6\]

^b^ obtained using CRYSTAL program\[^6\]
TABLE III. Total energies per unit cell for t-PA obtained in the present work, as a function of the number of nearest-neighbor unit cells included in the Coulomb series, \((M)\), and those included in the orthogonality region \(N\). For the sake of comparison, we also present results obtained with the CRYS\-TAL program\[37\]. In both the CRYS\-TAL and our calculations, the STO-3G basis set along with the optimized geometry reported in Sec.III.B were used. All the results are in atomic units.

| M  | \(3\)  | \(4\)  | \(5\)  | \(6\)  | \(7\)  |
|----|--------|--------|--------|--------|--------|
| 10 | -75.931783 | -75.931802 | -75.931807 | -75.931808 | -75.931808 |
| 20 | -75.943470 | -75.943489 | -75.943493 | -75.943494 | -75.943494 |
| 30 | -75.945851 | -75.945870 | -75.945874 | -75.945875 | -75.945876 |
| 40 | -75.946709 | -75.946728 | -75.946732 | -75.946733 | -75.946733 |
| 50 | -75.947112 | -75.947131 | -75.947135 | -75.947136 | -75.947136 |
| 75 | -75.947514 | -75.947533 | -75.947537 | -75.947538 | -75.947538 |
| 100| -75.947656 | -75.947675 | -75.947680 | -75.947681 | -75.947681 |
| 200| -75.947794 | -75.947813 | -75.947818 | -75.947819 | -75.947819 |
| 300| -75.947820 | -75.947839 | -75.947843 | -75.947844 | -75.947844 |
| 400| -75.947829 | -75.947848 | -75.947852 | -75.947853 | -75.947853 |
| 500| -75.947833 | -75.947852 | -75.947856 | -75.947857 | -75.947858 | -75.947597 |
TABLE IV. Total energies per unit cell for t-PA obtained in the present work, as a function of the number of nearest-neighbor unit cells included in the Coulomb series, \( M \), and those included in the orthogonality region \( N \). For the sake of comparison, we also present results obtained with the CRystal program\[^{\text{37}}\]. In both the CRystal and our calculations, the 6-31G-1\(^a\) basis set along with the optimized geometry reported in Sec. III B were used. All the results are in atomic units.

| This Work | CRYSTAL |
|-----------|---------|
| M | 3 | 4 | 5 | 6 | 7 |
| 30 | -76.865184 | -76.865198 | -76.865204 | -76.865207 | -76.865207 |
| 40 | -76.865813 | -76.865826 | -76.865832 | -76.865835 | -76.865835 |
| 50 | -76.866125 | -76.866138 | -76.866144 | -76.866146 | -76.866146 |
| 75 | -76.866449 | -76.866461 | -76.866467 | -76.866469 | -76.866469 |
| 100 | -76.866566 | -76.866578 | -76.866584 | -76.866586 | -76.866586 |
| 200 | -76.866682 | -76.866694 | -76.866700 | -76.866702 | -76.866702 |
| 300 | -76.866703 | -76.866715 | -76.866722 | -76.866724 | -76.866724 |
| 400 | -76.866711 | -76.866723 | -76.866729 | -76.866731 | -76.866731 |
| 500 | -76.866714 | -76.866727 | -76.866733 | -76.866735 | -76.866735 |

\(^a\) See section Sec. III B for explanation.
TABLE V. A summary of our HF results on t-PA with the STO-3G basis set and its comparison with the results of other authors. Our results are results of calculations performed with $N = 7$ and $M = 500$. The bond lengths are expressed in the units of Å, the bond angles are in degrees, the total energy per C$_2$H$_2$ unit ($E_{\text{total}}$) is in Hartrees. The bottom four entries in this table are results of Teramae’s calculations performed using different cutoff scheme for the Coulomb series and have been taken from table 12 of Teramae’s paper.

| Author      | $r_1$  | $r_2$  | $\Delta r$ | $R_{\text{CH}}$ | $\alpha$ | $E_{\text{total}}$ |
|-------------|-------|-------|------------|-----------------|---------|-------------------|
| This work$^a$ | 1.489 | 1.326 | 0.163 | 1.09$^b$ | 124.1 | -75.947858 |
| Dovesi$^c$  | 1.486 | 1.329 | 0.157 | 1.09$^b$ | 124.4 | -75.946061 |
| Karpfen et al.$^d$ | 1.477 | 1.327 | 0.15 | 1.09$^b$ | 124.2 | -75.948 |
| Suhai$^e$   | 1.471 | 1.328 | 0.143 | 1.08 | 124.0 | -75.947283 |
| Teramae$^f$ | 1.477 | 1.326 | 0.151 | 1.08 | 124.0 | -75.947935 |
| Teramae$^g$ | 1.477 | 1.326 | 0.151 | 1.08 | 124.1 | -75.948581 |
| Teramae$^h$ | 1.488 | 1.324 | 0.164 | 1.09 | 125.0 | -75.926695 |
| Teramae$^i$ | 1.475 | 1.326 | 0.149 | 1.08 | 123.9 | -75.952922 |

$^a$ Using a lobe representation of the STO-3G basis set.
$^b$ Held fixed at the experimental geometry.$^{43}$
$^c$ Ref.$^{10}$
$^d$ Ref.$^{4}$
$^e$ Ref.$^{9}$
$^f$ Obtained using the so-called Namur cutoff of the Coulomb series proposed by the Namur group.$^{11}$
$^g$ Obtained using the cell-wise cutoff scheme for the Coulomb series proposed by Karpfen.$^{47}$
$^h$ Obtained using the symmetric cutoff scheme for the Coulomb series proposed by Kertesz et al.$^{48}$
$^i$ Obtained using the modified symmetric cutoff scheme for the Coulomb series proposed by Teramae himself.$^{13}$
TABLE VI. A summary of our HF results on t-PA with the 6-31G** basis set and its comparison with the corresponding calculations performed by us with the CRystAL program and the results of other authors. To optimize the geometry with our code, we performed a series of calculations with varying geometry parameters with $N = 3$ and $M = 75$. Experimental values are also listed for comparison. The lengths are expressed in the units of Å, the bond angles are in degrees, the total energy per C\(_2\)H\(_2\) unit ($E_{\text{total}}$) is in Hartrees while the cohesive energy per CH unit ($E_{\text{coh}}$) is in eV.

|         | $r_1$  | $r_2$  | $\Delta r$ | $\alpha$ | $E_{\text{total}}$ | $E_{\text{coh}}$ |
|---------|--------|--------|------------|----------|---------------------|------------------|
| This work\(^a,b\) | 1.457  | 1.336  | 0.121      | 124.2    | -76.8881            | 7.32             |
| CRystal \(^b\)     | 1.464  | 1.333  | 0.131      | 124.2    | -76.8881            | 7.32             |
| Yu et al. \(^b,c\) | 1.458  | 1.335  | 0.123      | 124.1    | -76.8956            | 7.24             |
| Suhai \(^d\)       | 1.456  | 1.339  | 0.117      | 123.9    | -76.9025            | 7.26\(^c\)       |
| Exp. \(^f\)        | 1.45   | 1.36   | 0.09       | 121.7    | —                   | —                |
| Exp. \(^g\)        | 1.44   | 1.36   | 0.08       | —        | —                   | —                |
| Exp. \(^h\)        | 1.45±0.01 | 1.38±0.01 | 0.07      | —        | —                   | —                |

\(^a\) Performed with the lobe representation of the 6-31G** basis set described in the text.
\(^b\) C-H bond distance held fixed at the experimental value 1.09 Å\(^43\).
\(^c\) Ref.\(^25\). Yu et al. used a basis set of “valence double zeta + polarization” type.
\(^d\) Ref.\(^9\). Suhai used an extended basis set of “double zeta + polarization” type. He optimized the C-H bond distance also to obtain 1.08 Å.
\(^e\) Since Suhai’s paper\(^9\) does not provide any data on cohesive energies, we computed it by subtracting, from his value of $E_{\text{total}}$ quoted above, the atomic HF energies of C and H computed with the basis set used by him.
\(^f\) Ref.\(^43\).
\(^g\) Ref.\(^45\).
\(^h\) Ref.\(^46\).
A. Shukla et al.: Fig 1
