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Fourier Representation Method for Electronic Structures of Linear Polymers

II. Linear Chain of Hydrogen Atoms*

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The Fourier representation method described in the previous paper of this series is used to make electronic structure calculations for a linear chain of equally spaced hydrogen atoms. The electronic wavefunction is assumed to be a determinant of doubly-occupied crystal orbitals of modulated-plane-wave type, built from one $1s$ Slater-type orbital of screening parameter ζ centered on each atom. The energy is calculated from the electrostatic zero-order Hamiltonian with exact evaluation of all Coulomb and exchange contributions, and is optimized with respect to the lattice spacing and ζ value. Good agreement with work by others is noted, indicating a near-equivalence of modulated-plane-wave and tight-binding wavefunctions for this half-filled-valence-band system. The linear chain is calculated to be far more stable than cubic three-dimensional hydrogen crystals. This fact sheds light on the unusually large calculated nearest-neighbor distances in the cubic crystals, and is related to a suggestion that under certain conditions the most stable structure for solid atomic hydrogen may be of lower symmetry than cubic.

Key words: Polymers, linear ~

1. Introduction

In the past ten years a large number of theoretical investigations in research areas ranging from physics to biochemistry have been devoted to systems which can be thought of as one-dimensional crystals. Crystalline polymers (such as polyethylene

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[*] The previous paper of this series: Harris, F. E.: J. Chem. Phys. **56**, 4422 (1972) [1].

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or nylon) play an important role as plastics and fibers, biopolymers (such as DNA, RNA, and polypeptides) are of fundamental importance in life mechanisms, and highly anisotropic one-dimensional conductors (such as TTF-TCNQ) constitute a new challenge for modern technology [2, 3]. To understand the various physical and chemical properties of such systems, in particular their conductivities, conformational properties, and catalytic activity, it is necessary to have a rather detailed knowledge of their electronic structures. Thus far such knowledge has most frequently been adduced theoretically by empirical or semiempirical methods, and in favorable cases confirmed experimentally by techniques such as X-ray photoelectron spectroscopy.

The successes of such empirical theoretical techniques as the extended Hückel method, and of semiempirical procedures such as the CNDO and INDO methods, have affirmed the validity of conventional energy band schemes in describing [4] and predicting [5, 6] the electronic spectra of one-dimensional periodic systems. However, because of the crude approximations and arbitrary simplifications inherent in empirical and semiempirical approaches, these approaches are sometimes found to yield unreliable results [4]. There is therefore a continuing need for more firmly based methods which could be applied at least to some representative one-dimensional systems. The results of such prototype studies should be helpful in testing and comparing the data produced by simpler and cheaper techniques.

It is generally accepted that the Hartree–Fock method gives a rather satisfactory representation of the ground-state properties of typical closed-shell molecular systems. Several attempts have already been made to apply conventional Hartree–Fock techniques to polymers [7–12]. The common feature of these approaches is that they are direct extensions to infinite systems of the LCAO-MO-SCF method originally deduced by Roothaan and Hall for molecules. One class of methods treats clusters containing large but finite numbers of atoms by procedures designed for molecules; the remaining studies proceed by forming Bloch-wave crystal orbitals for a formally infinite crystal. Calculations of the latter type are usually referred to as LCAO-SCF-CO (linear combination of atomic orbitals-self consistent field-crystal orbitals). A recent review of the work in this area is provided in Ref. [3].

Here we want to report on an alternative approach to a description of polymers at the Hartree–Fock level. Our approach differs from the LCAO-based methods in that the crystal orbitals, while constructed using atomic orbitals, are not linear combinations thereof, but are instead sums of such orbitals modulated by a plane-wave phase factor. Such "modulated-plane-wave" orbitals have been found useful in studies of three-dimensional crystals possessing half-filled bands, and may therefore be expected also to be suitable for partially-filled bands in linear polymers. In calculational techniques, our approach also differs from most preceding studies through the systematic application of Fourier representation methods and the exploitation of lattice orthogonality relations. These procedures were found to simplify considerably the calculations for three-dimensional crystals, eliminating completely the multicenter integral problem encountered in direct-space approaches [13, 14]. They also yield a physically appealing partitioning of the total energy into easily interpretable, individually convergent contributions. In addition, calculations can be conveniently carried out in this way for wavefunctions based on any type of atomic orbital whose Fourier transform is known. This feature makes practical the use of Slater-type orbitals as well as Gaussians, an alternative not available with the usual LCAO-SCF-CO methods. While the above calculational advantages could also be realized by applying Fourier techniques to LCAO wavefunctions, the procedure is simpler when applied to the modulated-plane-wave functions. Many of the steps needed to carry out such calculations for linear polymers have already been discussed by one of the authors [1, 15].

It is our objective to illustrate the approach of this paper with a calculation for a simple model system. The system we have chosen is the infinite linear chain of equally spaced hydrogen atoms. Although not an experimentally accessible system, it is a useful prototype because a number of relevant comparable calculations have previously been reported. We will find it of interest to compare our calculations with crystal-orbital and atomic-cluster calculations of linear hydrogen by other authors [11, 12], and also to make a comparison with three-dimensional atomic-hydrogen lattices [16, 17]. The comparison with the three-dimensional structures will be found to lead naturally to a conjecture as to the most stable structure for the hypothetical metallic atomic-hydrogen crystal.

2. Problem Formulation

Consider a one-dimensional periodic lattice consisting of a macroscopic number, N, of unit cells of length a, with a proton fixed at each lattice point and an equal number of electrons distributed along the chain. The electrons are assumed to doubly occupy a set of one-electron crystal orbitals of Bloch type, constructed from atomic orbitals ϕ centered on the protons. Letting $|k\rangle$ denote the crystal orbital of Bloch wave number k, we write

$$|k\rangle = e^{2\pi i a^{-1} k z} \sum_{\mu}' \phi(\boldsymbol{r} - \mu a \hat{\boldsymbol{z}}) \tag{1}$$

where $\boldsymbol{r}$ is the position vector measured from an arbitrary but fixed origin, $\hat{\boldsymbol{z}}$ is a unit vector in the direction of lattice periodicity, and μ and other Greek-letter indices refer to the N points of a lattice of unit length (i.e., to ..., -2, -1, 0, 1, 2, . . .).

The crystal orbitals defined by Eq. (1) are not of the conventional LCAO or "tight-binding" type, but are of the sort we refer to as "modulated-plane-wave" (MPW). These orbitals have the symmetry under translation by $a\hat{\boldsymbol{z}}$ which is required by Bloch's theorem, but, unlike tight-binding functions, they are not periodic in k. In the notation we are using, the Brillouin zone corresponds to a unit range of k, from $-\frac{1}{2}$ to $+\frac{1}{2}$, and the reciprocal lattice has cell length $2\pi/a$. Crystal orbitals within the Brillouin zone are caused to be orthogonal by the symmetry properties inherent in Eq. (1). One-half the crystal orbitals within the Brillouin zone are occupied, and for the ground electronic state the occupied orbitals have k values in the range $-\frac{1}{4} \leqslant k \leqslant +\frac{1}{4}$.

Eq. (1) can conveniently be used with any atomic orbital ϕ whose Fourier transform is amenable to manipulation; its use need not be restricted to orbitals for which multicenter integrals are easily reduced. In the present application, we have chosen ϕ to be the 1*s* Slater-type atomic orbital

$$\phi=(\zeta^3/\pi)^{1/2}\,e^{-\zeta r} \tag{2}$$

In addition to the general arguments in its favor, this choice has the advantage of facilitating comparison with results for atomic hydrogen, the hydrogen molecule, and hydrogen cluster calculations.

In atomic units (length in bohrs, energy in hartrees), the usual zero-order non-relativistic Hamiltonian can be cast in the form

$$H=\sum_{i=1}^{N}(-\tfrac{1}{2}\nabla_i^2)+\sum_{1\leqslant i<j\leqslant N}(h\boldsymbol{r}_i,\boldsymbol{r}_j) \tag{3}$$

with

$$h(\boldsymbol{r}_1,\boldsymbol{r}_2)=r_{12}^{-1}-\frac{1}{N}\sum_{\mu}|\boldsymbol{r}_1-\mu a\hat{\boldsymbol{z}}|^{-1}-\frac{1}{N}\sum_{\mu}|\boldsymbol{r}_2-\mu a\hat{\boldsymbol{z}}|^{-1}+\frac{1}{N_2}\sum_{\substack{\mu\nu\\ \mu\neq\nu}}|(\mu-\nu)a\hat{\boldsymbol{z}}|^{-1} \tag{4}$$

Considering the double occupancy of the crystal orbitals and the antisymmetry requirement on the many-electron wavefunction, the expectation value of the total energy takes the form

$$\begin{aligned}E={}&2N\int_{-1/4}^{+1/4}dk\,\frac{\langle k|-\frac{1}{2}\nabla^2|k\rangle}{\langle k|k\rangle}\\&+2N^2\int_{-1/4}^{+1/4}dk\int_{-1/4}^{+1/4}dk'\,\frac{\langle kk'|h|kk'\rangle-\frac{1}{2}\langle kk'|r_{12}^{-1}|k'k\rangle}{\langle k|k\rangle\langle k'|k'\rangle}\end{aligned} \tag{5}$$

3. Integrals

The first step toward the calculation of E is the evaluation of the integrals occurring on the right hand side of Eq. (5). The techniques to be used depend upon the properties of Fourier transforms. We find it convenient to define the Fourier transform $f^T(\boldsymbol{q})$ of a function $f(\boldsymbol{r})$ so that the transform variable is dimensionless and scaled like Bloch wave numbers:

$$f^T(\boldsymbol{q})=\int d\boldsymbol{r}\,e^{2\pi i a^{-1}\boldsymbol{q}\cdot\boldsymbol{r}}f(\boldsymbol{r}) \tag{6}$$

Other relationships we shall find essential, in a notation consistent with Eq. (6), are the following:

$$\int d\boldsymbol{r}_1\,d\boldsymbol{r}_2\,f(\boldsymbol{r}_1)r_{12}^{-1}g(\boldsymbol{r}_2-\boldsymbol{R})=\frac{1}{\pi a}\int\frac{d\boldsymbol{q}}{q_2}f^T(\boldsymbol{q})g^T(-\boldsymbol{q})\,e^{-2\pi i a^{-1}\boldsymbol{q}\cdot\boldsymbol{R}} \tag{7}$$

$$[f(\mathbf{r})g(\mathbf{r}-\mathbf{R})]^T(\mathbf{q})=\frac{1}{a^3}\int d\mathbf{p}\, f^T(\mathbf{p})\,g^T(\mathbf{q}-\mathbf{p})\; e^{2\pi i a^{-1}(\mathbf{q}-\mathbf{p})\cdot\mathbf{R}} \tag{8}$$

$$\int d\mathbf{r}\, f(\mathbf{r})\,g(\mathbf{r}-\mathbf{R})=\frac{1}{a^3}\int d\mathbf{p}\, f^T(\mathbf{p})\,g^T(-\mathbf{p})\; e^{-2\pi i a^{-1}\mathbf{p}\cdot\mathbf{R}} \tag{9}$$

$$[-\tfrac{1}{2}\nabla^2 f(\mathbf{r})]^T(\mathbf{p})=\frac{2\pi^2}{a^2}\,p^2 f^T(\mathbf{p}) \tag{10}$$

$$\sum_{\nu=-\infty}^{\infty} e^{-2\pi i p_z \nu}=\sum_{\nu=-\infty}^{\infty}\delta(p_z-\nu) \tag{11}$$

$$\phi^T(p)=\frac{(2a)^{3/2}}{\pi}\,\frac{\alpha^{5/2}}{(p^2+\alpha^2)^2},\quad \alpha=\frac{a\zeta}{2\pi} \tag{12}$$

In these equations the $\mathbf{r}$ and $\mathbf{p}$ or $\mathbf{q}$ integrations are over a full three-dimensional space. Eq. (7) is the reduction of the electron repulsion integral introduced by Bonham, Peacher and Cox [18]; Eq. (8) is a standard form of the Fourier convolution theorem; Eq. (9) is a consequence of the convolution and inversion theorems; Eq. (10) is a standard result [19]; and Eq. (11) is a lattice orthogonality relation [20]. Eq. (12) gives the transform of the 1*s* STO.

We proceed now to the evaluation of the various integrals. We shall find that many of the results can be expressed in terms of Fourier transforms of lattice sums of orbital products. We therefore introduce the definition

$$\Phi^T(\mathbf{q})=\sum_{\nu=-\infty}^{\infty}\langle\phi(\mathbf{r})|\; e^{2\pi i a^{-1}\mathbf{q}\cdot\mathbf{r}}|\phi(\mathbf{r}-\nu a\hat{\mathbf{z}})\rangle \tag{13}$$

The evaluation of $\Phi^T(\mathbf{q})$ will be presented after the discussion of the integrals in which it occurs.

3.1. Overlap Integral

The overlap integral for the MPW functions of Eq. (1) is

$$\begin{aligned}\langle k|k\rangle &=\sum_{\mu\nu}\langle e^{2\pi i a^{-1}kz}\phi(\mathbf{r}-\nu a\hat{\mathbf{z}})|\; e^{2\pi i a^{-1}kz}\phi(\mathbf{r}-\mu a\hat{\mathbf{z}})\rangle\\ &=N\sum_{\mu}\langle\phi(\mathbf{r})|\phi(\mathbf{r}-\mu a\hat{\mathbf{z}})\rangle\\ &=N\Phi^T(0)\end{aligned} \tag{14}$$

as may be seen by comparison with Eq. (13). An explicit expression for $\Phi^T(0)$ is given in Eq. (23). We note that because of the form chosen for $|k\rangle$, the integral $\langle k|k\rangle$ is independent of k.

3.2. Kinetic Energy Integral

The kinetic energy integral satisfies the equation

$$\langle k|-\tfrac{1}{2}\nabla^2|k\rangle=\frac{2\pi^2k^2N}{a^2}\sum_{\nu}\langle\phi(\mathbf{r})|\phi(\mathbf{r}-\nu a\hat{\mathbf{z}})\rangle+N\sum_{\nu}\langle\phi(\mathbf{r})-\tfrac{1}{2}\nabla^2|\phi(\mathbf{r}-\nu a\hat{\mathbf{z}})\rangle \tag{15}$$

The first term of Eq. (15) results from application of ∇^2 to $\exp(2\pi i a^{-1} kz)$; the second term from its application to $\phi(\boldsymbol{r}-va\hat{\boldsymbol{z}})$. The term in which each of these factors is differentiated once vanishes due to symmetry. The sum in the first term of Eq. (15) is simply $\Phi^T(0)$; the second term is more complex but may be processed using Eqs. (9), (10), and (12). We then have

$$\langle k|-\tfrac{1}{2}\nabla^2|k\rangle=\frac{2\pi^2 N}{a^2}\left[k^2\Phi^T(0)+\frac{8\alpha^5}{\pi^2}\sum_v\int\frac{p^2\,d\boldsymbol{p}}{(p^2+\alpha^2)^4}\,e^{-2\pi i v p_z}\right] \tag{16}$$

We next express $\boldsymbol{p}$ in the cylindrical coordinates (t,θ,p_z), where $t=(p_x^2+p_y^2)^{1/2}$, $\theta=\tan^{-1}(p_y/p_x)$, and $d\boldsymbol{p}=t\,dt\,d\theta\,dp_z$, performing the θ integration (which is trivial) and the p_z integration after substitution of Eq. (11). The result is

$$\langle k|-\tfrac{1}{2}\nabla^2|k\rangle=\frac{2\pi^2 N}{a^2}\left[k^2\Phi^T(0)+\frac{16\alpha^5}{\pi}\sum_v\int_0^\infty\frac{t(t^2+v^2)\,dt}{(t^2+v^2+\alpha^2)^4}\right] \tag{17}$$

Finally, we integrate over t, leaving summations over v which we have previously encountered and which can be evaluated in closed form (see Appendix A of Ref. [17]). We ultimately reach

$$\begin{aligned}\langle k|-\tfrac{1}{2}\nabla^2|k\rangle=\frac{2\pi^2 N}{a^2}\,[k^2\Phi^T(0)&\\+\alpha^2(\operatorname{ctnh}(\pi\alpha)+\pi\alpha[1-\tfrac{2}{3}\pi\alpha\operatorname{ctnh}(\pi\alpha)]\operatorname{csch}^2(\pi\alpha))]&\end{aligned} \tag{18}$$

3.3. Coulomb and Exchange Integrals

In the first paper of this series [1] it was shown how the Coulomb and exchange contributions to the potential energy could be reduced to expressions involving $\Phi^T(\boldsymbol{q})$. In order to avoid the introduction of divergences in the expression for the Coulomb energy, it was found to be necessary to use care in the grouping of the various terms. It was then possible to use Eq. (7) to obtain the result

$$\begin{aligned}\langle kk'|h|kk'\rangle=&-\frac{2N}{a}\ln(2\pi\alpha)\Phi^T(0)\Phi^T(0)+\frac{N}{\pi a}\int_0^{2\pi}d\varphi\int_0^\infty s\,ds\sum_\mu(s^2+\mu^2)^{-1}\\&\times\Bigg[\Phi^T(\boldsymbol{q}_\mu)\Phi^T(-\boldsymbol{q}_\mu)-\Phi^T(\boldsymbol{q}_\mu)\Phi^T(0)-\Phi^T(0)\Phi^T(-\boldsymbol{q}_\mu)\\&+\delta_{\mu 0}\frac{\alpha^2}{s^2+\alpha^2}\Phi^T(0)\Phi^T(0)\Bigg]\end{aligned} \tag{19}$$

We have introduced the notation $\boldsymbol{q}_\mu$ to stand for the point $\boldsymbol{q}$ with cylindrical coordinates s, φ, μ; we shall later use $\boldsymbol{q}_0$ to refer to the point $(s,\varphi,0)$.

The exchange energy reduces without difficulties to the expression

$$\langle kk'|r_{12}^{-1}|k'k\rangle=\frac{N}{\pi a}\int_0^{2\pi}d\varphi\int_0^\infty s\,ds\sum_\mu\frac{\Phi^T(\boldsymbol{q}_\mu)\Phi^T(-\boldsymbol{q}_\mu)}{s^2+(\mu+k-k')^2} \tag{20}$$

Evaluation of $\Phi^T(\boldsymbol{q}_\mu)$ is discussed in the subsection to follow. Eqs. (19) and (20) show that the Coulomb integral $\langle kk'|h|kk'\rangle$ is independent of k and k', but that the exchange integral is not.

3.4. *Evaluation of $\Phi^T(\boldsymbol{q})$*

The foregoing subsections show that we will need to evaluate $\Phi^T(\boldsymbol{q})$ for $\boldsymbol{q}=0$ and for nonzero values of integer or zero z component (in cylindrical coordinates, points (s, φ, μ)). We consider first the simpler case $\boldsymbol{q}=0$. Referring to the definition for $\Phi^T(\boldsymbol{q})$ given in Eq. (13) and there setting $\boldsymbol{q}=0$, we apply Eqs. (9) and (12) to obtain

$$\Phi^T(0)=\frac{8\alpha^5}{\pi^2}\sum_{\nu}\int_0^{\infty}\frac{d\boldsymbol{p}}{(p^2+\alpha^2)^4}\,e^{-2\pi i\nu p_z} \tag{21}$$

Converting $\boldsymbol{p}$ to cylindrical coordinates t, θ, p_z, using Eq. (11), and integrating over θ and p_z, we find

$$\Phi^T(0)=\frac{16\alpha^5}{\pi}\sum_{\nu}\int_0^{\infty}\frac{t\,dt}{(t^2+\nu^2+\alpha^2)^4} \tag{22}$$

Carrying out the t integration and the ν summation [17], we have the final result

$$\Phi^T(0)=\operatorname{ctnh}(\pi\alpha)+\pi\alpha(1+\tfrac{2}{3}\pi\alpha\operatorname{ctnh}(\pi\alpha))\operatorname{csch}^2(\pi\alpha) \tag{23}$$

Proceeding next to nonzero $\boldsymbol{q}$ values, we combine Eqs. (8), (12) and (13) to obtain the preliminary formula

$$\Phi^T(\boldsymbol{q})=\frac{8\alpha^5}{\pi^2}\sum_{\nu}\int_0^{\infty}\frac{d\boldsymbol{p}\,e^{2\pi i(q_z-p_z)\nu}}{(p^2+\alpha^2)^2(|\boldsymbol{q}-\boldsymbol{p}|^2+\alpha^2)^2} \tag{24}$$

Introducing cylindrical coordinates $\boldsymbol{q}=(s, \varphi, \mu)$ and $\boldsymbol{p}=(t, \theta, p_z)$ (remember that we only need $\boldsymbol{q}$ values of integer or zero z component), Eq. (24) becomes

$$\Phi^T(s,\varphi,\mu)=\frac{8\alpha^5}{\pi^2}\sum_{\nu}\int_{-\infty}^{+\infty}dp_z\,e^{2\pi i(\mu-p_z)\nu}\int_0^{\infty}t\,dt\int_0^{2\pi}d\theta \\ \times\frac{1}{(t^2+p_z^2+\alpha^2)^2[s^2+t^2-2st\cos(\theta-\varphi)+(\mu-p_z)^2+\alpha^2]^2} \tag{25}$$

We continue by using Eq. (11) and integrating over p_z, then carrying out the θ integration. Note that, due to the symmetry of the problem, Φ^T does not actually depend upon φ. We then have for nonzero s (changing the integration variable from t to $u=t^2$)

$$\Phi^T(s,\varphi,\mu)=\frac{8\alpha^5}{\pi}\sum_{\nu}[(A+C)I_1+I_0]\quad(s>0) \tag{26}$$

with

$$I_n=\int_0^\infty \frac{du}{(u-A)^{n+1}(u^2-2Bu+C^2)^{3/2}} \tag{27}$$

and $A=-(\mu+\nu)^2-\alpha^2$, $B=s^2-(\nu^2+\alpha^2)$, $C=s^2+\nu^2+\alpha^2$

We now evaluate I_1 and I_0, and to the extent possible reduce the summations to closed forms. For nonzero s, we obtain the final formula

$$\begin{aligned}\Phi^T(s,\varphi,\mu)=\frac{8\alpha^5}{\pi}\Bigg\{&\frac{\pi}{2(s^2+\mu^2)}\\ &\times\Bigg[\frac{(\frac{1}{4}\mu^2-\beta^2+\alpha^2)g_1(\pi\beta)+(\frac{1}{4}\mu^2-\alpha^2+\beta^2)\alpha^{-1}\operatorname{ctnh}(\pi\alpha)}{[\frac{1}{4}\mu^2+(\beta-\alpha)^2][\frac{1}{4}\mu^2+(\beta+\alpha)^2]}\\ &\qquad-\frac{3g_2(\pi\beta)}{s^2+\mu^2+4\alpha^2}\Bigg]\\ &+\sum_\nu \gamma^{-3}[1+3(B-A)(A+C)\gamma^{-2}]\ln\left(\frac{C^2+\gamma C-AB}{A(B-A-\gamma)}\right)\Bigg\}\quad(s>0)\end{aligned} \tag{28}$$

with

$$\beta=\left(\frac{s^2}{4}+\frac{\alpha^2s^2}{\mu^2+s^2}\right)^{1/2},$$

$$\gamma=(A^2+C^2-2AB)^{1/2},$$

$$\begin{aligned}g_1(\pi\beta)&=\beta^{-1}\operatorname{ctnh}(\pi\beta)\text{ for }\mu\text{ even}\\ &=\beta^{-1}\tanh(\pi\beta)\text{ for }\mu\text{ odd,}\\ g_2(\pi\beta)&=\beta^{-1}\operatorname{ctnh}(\pi\beta)+\pi\operatorname{csch}^2(\pi\beta)\text{ for }\mu\text{ even}\\ &=\beta^{-1}\tanh(\pi\beta)-\pi\operatorname{sech}^2(\pi\beta)\text{ for }\mu\text{ odd}\end{aligned}$$

We were not able to reduce the logarithm-containing sum to a closed analytical expression. The formula corresponding to Eq. (28) when $s=0$ is not difficult to derive but will not be needed because we use $\Phi^T(s,\varphi,\mu)$ in numerical integration formulas not requiring its value for zero s but nonzero μ.

4. Total Energy

We are now ready to evaluate the expression for the total energy E given in Eq. (5). We may divide E into kinetic, Coulomb, and exchange contributions.

Taking first the kinetic energy E_K, from Eqs. (14) and (18) we have

$$\begin{aligned}E_K&=2N\left(\frac{2\pi^2}{a^2}\right)\int_{-1/4}^{+1/4}dk\left(k^2+\alpha^2\frac{\operatorname{ctnh}(\pi\alpha)+\pi\alpha[1-\frac{2}{3}\pi\alpha\operatorname{ctnh}(\pi\alpha)]\operatorname{csch}^2(\pi\alpha)}{\operatorname{ctnh}(\pi\alpha)+\pi\alpha[1+\frac{2}{3}\pi\alpha\operatorname{ctnh}(\pi\alpha)]\operatorname{csch}^2(\pi\alpha)}\right)\\ &=N\left(\frac{2\pi}{a}\right)^2\left[\frac{1}{96}+\frac{\alpha^2}{2}\left(1-\frac{\frac{4}{3}\alpha^2\pi^2\operatorname{ctnh}(\pi\alpha)\operatorname{csch}^2(\pi\alpha)}{\operatorname{ctnh}(\pi\alpha)+\pi\alpha[1+\frac{2}{3}\pi\alpha\operatorname{ctnh}(\pi\alpha)]\operatorname{csch}^2(\pi\alpha)}\right)\right]\end{aligned} \tag{29}$$

Because of the MPW choice for $|k\rangle$ the kinetic energy is naturally divided into free-electron and local contributions.

We next consider the Coulomb contribution E_C. Because $\langle kk'|h|kk'\rangle$ (cf. Eq. (19)) does not depend upon k, k', or the angular coordinate φ, the integrations over these quantities are trivial. The remaining integration, over s, is well behaved and may be obtained by a straightforward numerical quadrature. Recognizing that $\Phi^T(-\boldsymbol{q})=\Phi^T(\boldsymbol{q})$, we have the working formula

$$E_c=\frac{N}{a\Phi^T(0)\Phi^T(0)}\left\{\int_0^\infty \frac{ds}{s}\left(\Phi^T(\boldsymbol{q}_0)\Phi^T(\boldsymbol{q}_0)-\Phi^T(0)\left[2\Phi^T(\boldsymbol{q}_0)-\frac{\alpha^2}{s^2+\alpha^2}\Phi^T(0)\right]\right)\right.$$
$$\left.+2\sum_{\mu=1}^{\infty}\int_0^\infty \frac{sds}{s^2+\mu^2}[\Phi^T(\boldsymbol{q}_\mu)\Phi^T(\boldsymbol{q}_\mu)-2\Phi^T(\boldsymbol{q}_\mu)\Phi^T(0)]\right\}-\frac{N}{a}\ln(2\pi\alpha) \tag{30}$$

Eq. (30) may be given a simple physical interpretation if we note that its last term describes the entire Coulomb energy in the limit of a uniform electron distribution. The other terms describe contributions associated with the nonuniformity of the electron distribution, those quadratic in $\boldsymbol{q}_\mu$ or $\boldsymbol{q}_0$ giving the modification of the electron repulsion energy and those linear in these variables giving the modification of the electron-nuclear attraction energy.

Finally, we consider the exchange energy, E_X. Although $\langle kk'|r_{12}^{-1}|k'k\rangle$ does depend upon k and k', an examination of Eq. (20) indicates that the k and k' integrations will all be of the form

$$\int_{-1/4}^{+1/4} dk \int_{-1/4}^{+1/4} dk' \frac{s}{s^2+(\mu+k-k')^2}=(\mu+\tfrac{1}{2})\tan^{-1}\left(\frac{\mu+\frac{1}{2}}{s}\right)+(\mu-\tfrac{1}{2})\tan^{-1}\left(\frac{\mu-\frac{1}{2}}{s}\right)$$
$$-2\mu\tan^{-1}\frac{\mu}{s}+\frac{s}{2}\ln\left(\frac{(s^2+\mu^2)^2}{[s^2+(\mu+\frac{1}{2})^2][s^2+(\mu-\frac{1}{2})^2]}\right) \tag{31}$$

Although the integrand on the left side of Eq. (31) becomes singular at $s=\mu=0$ and $k=k'$, the right hand side shows the integral to be well conditioned and susceptible to the usual methods of numerical quadrature. This point is illustrated by the numerical values of this integral given in Table 1.

Table 1. Numerical values of the exchange-energy integral, Eq. (31)

s	$\mu=0$	$\mu=1$	$\mu=2$	$\mu=3$
0.00	1.57080	0.0	0.0	0.0
0.01	1.47255	2.87641×10^{-3}	6.45366×10^{-4}	2.81705×10^{-4}
0.05	1.24037	1.43334×10^{-2}	3.22475×10^{-3}	1.40814×10^{-3}
0.10	1.04759	2.83678×10^{-2}	6.43650×10^{-3}	2.81386×10^{-3}
0.50	4.38825×10^{-1}	1.07756×10^{-1}	3.02362×10^{-2}	1.36925×10^{-2}
1.00	2.40504×10^{-1}	1.27466×10^{-1}	5.09303×10^{-2}	2.52742×10^{-2}
2.00	1.23729×10^{-1}	9.98212×10^{-2}	6.28214×10^{-2}	3.86800×10^{-2}
5.00	4.99170×10^{-2}	4.80119×10^{-2}	4.30756×10^{-2}	3.67672×10^{-2}
10.00	2.49896×10^{-2}	2.47427×10^{-2}	2.40303×10^{-2}	2.29299×10^{-2}

With the aid of Eq. (31), we find the following working formula for the exchange energy, in which the s integration is to be carried out numerically:

$$E_X = -\frac{2N}{a\Phi^T(0)\Phi^T(0)} \left\{ \int_0^\infty ds\, \Phi^T(q_0)\Phi^T(q_0) \left[\tan^{-1}\left(\frac{1}{2s}\right) + s \ln\left(\frac{s^2}{s^2+\frac{1}{4}}\right)\right] \right.$$

$$+ \sum_{\mu=1}^{\infty} \int_0^\infty ds\, \Phi^T(q_\mu)\Phi^T(q_\mu)\left[2(\mu+\tfrac{1}{2})\tan^{-1}\left(\frac{\mu+\frac{1}{2}}{s}\right) + 2(\mu-\tfrac{1}{2})\tan^{-1}\left(\frac{\mu-\frac{1}{2}}{s}\right)\right.$$

$$\left.\left. - 4\mu\tan^{-1}\frac{\mu}{s} + s\ln\frac{(s^2+\mu^2)^2}{[s^2+(\mu+\frac{1}{2})^2][s^2+(\mu-\frac{1}{2})^2]}\right]\right\} \tag{32}$$

Eq. (32) shows that the exchange energy consists of a free-electron-like contribution ($\mu=0$) and a correction term which takes into account the nonuniformity of the charge distribution.

Combining the various contributions, the total energy per atom will be

$$E/N = (E_K + E_C + E_X)/N. \tag{33}$$

5. Numerical Techniques and Computer Programming

In Sect. 3 the formula we derived for $\Phi^T(s, \varphi, \mu)$, Eq. (28), contains an unreduced summation with logarithmic summands. This summation is slowly convergent for small μ values when $s<1$, and we have found it advisable to accelerate its convergence by use of the Euler–MacLaurin summation formula [21]. The sum, whose terms we designate $f(v, \mu, s)$, is divided into three parts:

$$\sum_{v=-\infty}^{+\infty} f(v,\mu,s) = \sum_{v=n_a}^{n_b} f(v,\mu,s) + \sum_{v=n_b+1}^{+\infty} f(v,\mu,s) + \sum_{v=-\infty}^{n_a-1} f(v,\mu,s) \tag{34}$$

with n_a and n_b chosen to make the Euler–MacLaurin formula rapidly convergent for the last two partial sums. For the second partial sum, this formula is

$$\sum_{v=n_b+1}^{\infty} f(v,\mu,s) = \int_{n_b}^{\infty} f(v,\mu,s)\,dv - \tfrac{1}{2}f(n_b,\mu,s) - \tfrac{1}{12}f'(n_b,\mu,s)$$

$$+ \tfrac{1}{720}f^{(3)}(n_b,\mu,s) - \cdots \tag{35}$$

A corresponding formula applies to the third partial sum. In evaluating Eq. (34), advantage is taken of the symmetry properties of $f(v, \mu, s)$:

$$\begin{aligned} &f(v,\mu,s) = f(v,-\mu,s) \\ &f(|v|,\mu,s) = f(-|v|-|\mu|,\mu,s) \end{aligned} \tag{36}$$

The closed analytical portion of Eq. (28) also presents numerical difficulties when $\mu=0$ and s small ($<10^{-1}$). Under these conditions $\alpha\approx\beta$, and the square bracket on the right hand side of Eq. (28) may be rearranged to the form

$$\begin{aligned}\left[\quad\right] &= \frac{2\pi}{(\beta+\alpha)^2 \sinh(\pi\alpha)\sinh(\pi\beta)}\left(1+\frac{\pi^2}{6}(\beta-\alpha)^2+\frac{\pi^4}{120}(\beta-\alpha)^4+\cdots\right)\\ &\quad+\frac{\beta^{-1}\operatorname{ctnh}(\pi\beta)+\alpha^{-1}\operatorname{ctnh}(\pi\alpha)}{(\beta+\alpha)^2}-\frac{3g_2(\pi\beta)}{4\beta^2}\end{aligned} \tag{37}$$

Computer programs for calculating $\Phi^T(s, \varphi, \mu)$ and the total energy were written in FORTRAN for the Univac 1108 computer. The numerical quadratures and series expansions were adjusted to yield six significant figures in the final results. We found $\mu_{\max}=15$ to provide the desired precision. For the numerical integrations over s, we used ten-point Gauss–Legendre quadratures over the four separate intervals (0, 2), (2, 10), (10, 50), and (50, 100). More efficient schemes are undoubtedly possible but we were tentatively satisfied with that described. The time needed to calculate an individual $\Phi^T(s, \varphi, \mu)$ depended upon the parameter values, but was typically of the order of 50 msec. A complete calculation of the energy for a specified lattice spacing and Slater exponent required approximately 20 sec. The program output included the individual-μ contributions to the Coulomb and exchange energies, the values of E_K, E_C, and E_X, the virial ratio, and the total energy.

6. Results and Discussion

We made a number of calculations of the total energy of an infinite linear chain of hydrogen atoms by the method described in previous sections of this paper, varying the lattice spacing a and the STO screening parameter ζ to minimize the energy. We are confident of the numerical results to at least five significant figures in the total energy. The calculations for the optimum a and ζ values are presented in Table 2. As indicated earlier, these calculations are for a determinantal function based on doubly-occupied crystal orbitals of modulated-plane-wave type containing one 1s STO per atom.

In addition to giving total energy values, Table 2 contains information tending to corroborate our claim of numerical adequacy and permitting a more detailed interpretation of the results. In particular, we note the satisfactory convergence with summation index μ of the contributions to the Coulomb and exchange energy. We also observe that the virial ratio, $(E_C+E_X)/E_K$, is satisfactorily close to its theoretical value of -2. Looking at the two contributions to the Coulomb energy, we see that somewhat more than half of it can be attributed to that of a uniform electron distribution, the remainder being the effect of the actual nonuniformity. Comparing the $\mu=0$ and total exchange energies, we see that the nonuniformity increases (i.e., reduces the magnitude of) the exchange energy by about 2%.

There are a number of other calculations on linear hydrogen chains with which we can compare our current results. Calculations on clusters of hydrogen atoms have been reported by two groups; those of "Kislow" *et al.* [11] (the name is actually spelled Liskow) are based on ring configurations of up to 62 atoms, while those of Kertesz, Koller and Azman [12] are for a 30-atom linear array. Kertesz *et al.* also report a result based on conventional Bloch-wave orbitals (LCAO-SCF-CO). All these calculations are based on one 1*s* STO per atom, formed as a linear combination of Gaussian-type functions. LCAO-SCF-CO results have also been reported by Berggren and Martino [10], Calais [7], and André [9].

Table 2. Modulated-plane-wave calculations on infinite linear chain of equally spaced hydrogen atoms, at optimized lattice spacing $a = 1.78$ bohr and optimized STO screening parameter $\zeta = 1.78$. This calculation has total energy -0.52660 hartree/atom and virial ratio -2.003. All tabular entries are energy contributions, in hartree/atom

Contribution	Coulomb	Exchange	Kinetic
Total	−0.75376	−0.29765	+0.52482
Uniform-distribution	−0.43427	−0.30427	+0.12979
Total nonuniformity	−0.31949	+0.00662	+0.39503
Nonuniformity, individual-μ terms:			
$\mu = 0$	−0.277806	—	
1	−0.037014	+0.006501	
2	−0.003460	+0.000104	
3	−0.000745	+0.000013	
4	−0.000243	+0.000002	
5	−0.000101	+0.000001	
6	−0.000049	+0.000000	
7	−0.000027		
8	−0.000016		
9	−0.000010		
10	−0.000006		
11	−0.000004		
12	−0.000003		
13	−0.000002		
14	−0.000002		
15	−0.000001		

Table 3. Calculated energies (hartrees/atom) for linear chain of hydrogen atoms, at lattice spacing a (bohrs) and STO screening parameter ζ. The a and ζ values are optimal except for the first calculation of the present study

Method	a	ζ	E	Virial ratio
Cluster, 62-atom ring (Ref. [11])	1.886	1.130	−0.52978	
Cluster, 30-atom line (Ref. [12])	1.88	1.130	−0.52912	
LCAO crystal orbital (Ref. [12])	1.88	1.130	−0.52787	
MPW crystal orbital (this study)	1.88	1.130	−0.52385	−2.150
Optimized MPW crystal orbital (this study)	1.78	1.217	−0.52660	−2.003

The cluster and LCAO-SCF-CO calculations of the "Kislow" and Kertesz groups are presented in Table 3. This table also includes two calculations of the present study, one with the same a and δ parameters as were used in the studies by others, and one with the parameters we found to be optimum. The remaining previous calculations contain broken-symmetry orbitals to various extents and are not closely comparable to those reported here. The main difference between the cluster and crystal-orbital calculations is that the orbitals of the former are not restricted to be simple sums of the Bloch-wave type. This additional freedom appears to lower the energy by no more than about 0.002 hartrees/atom. The small difference between the two cluster calculations is of the wrong sign to be identified with the fact that the clusters are of different sizes; using the "Kislow" energies for different sized clusters the Kertesz energy would extrapolate to about -0.5285 hartrees/atom.

The present study shows the energy to be very little influenced by the use of modulated-plane-wave rather than LCAO crystal orbitals. This fact will be significant in the comparisons we shall make with calculations of three-dimensional atomic hydrogen lattices. We also note that the optimum lattice spacing and STO screening parameters are close to, but not identical with those found in the previous studies. The change in screening parameter can be directly attributed to the difference between MPW and LCAO crystal orbitals, as for nonzero Bloch wave numbers k the LCAO orbitals are more spatially inhomogeneous than are MPW orbitals of the same ζ. For an MPW orbital to provide a spatial distribution as similar as possible to that of an LCAO orbital of the same k, the MPW orbital would have to be constructed from atomic functions with a larger ζ value. Because even after this adjustment the MPW and LCAO wavefunctions are not identical, the optimum a values of the two calculations must differ slightly. The effect becomes more pronounced as k increases, and the comparison of MPW and LCAO results shows that these wavefunctions can still be made quite similar in a situation involving a half-filled valence band.

It is also of interest to compare the present calculations with previous studies of three-dimensional lattices. Harris, Kumar, and Monkhorst [16] have calculated optimum lattice spacings and energies/atom for simple cubic (sc), body-centered cubic (bcc), and face-centered cubic (fcc) atomic hydrogen crystals. For an MPW

Table 4. Comparison of modulated-plane-wave calculations on cubic and linear atomic hydrogen lattices. Nearest-neighbor distances δ in bohrs, energies in hartrees/atom

Calculation		δ	E
Cubic MPW: (Ref. [16])	sc	2.83	−0.463
	bcc	2.85	−0.467
	fcc	2.99	−0.468
Cubic Hartree-Fock: (Ref. [22])	sc	2.71	−0.477
Linear chain MPW (this study)		1.78	−0.527
Estimated correlation energy (Ref. [11])			−0.027

wavefunction based on one 1*s* STO per atom, their results are as shown in Table 4. Also given in Table 4 are more exact Hartree–Fock results for the sc atomic hydrogen crystal [22], the "Kislow" estimate of the correlation energy, and the optimized results of the present study. The one-STO MPW results on solid hydrogen are directly comparable with the linear polymer results, and unambiguously indicate a significant energetic destabilization accompanying the condensation of linear hydrogen chains into a solid of any cubic symmetry. The conclusion remains unaltered even if we compare the present linear-chain results with the best Hartree–Fock calculation on the solid. Furthermore, we note that the energy difference is large compared with any reasonable assumption as to possible differences in the correlation energies of the two systems.

The observations of the preceding paragraph may help to explain why the nearest-neighbor distances calculated for all the cubic solid hydrogen structures are so much larger than that in the linear chain. If we think of solid hydrogen as being formed by bringing together linear chains, there will be a repulsion between neighboring chains, and the optimum cubic configuration will have a larger intrachain spacing so as to increase the interchain separation. However, the data are also suggestive of a rather interesting alternative proposed by Brovman, Kagan, and Kholas [23, 24], namely that under certain conditions the most stable structure for three-dimensional atomic hydrogen may not be cubic at all, but may instead consist of linear filaments which are separated from each other by greater distances than that of nearest neighboring atoms of the same filament. An examination of this question will be the subject of another communication [25].

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