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Numerical solution of the Hartree-Fock equations for quasi-one-dimensional systems: Prototypical calculations on the $(\text{—H—})_x$ chain

Mireille Defranceschi
Laboratoire de Chimie, Ecole Normale Suprieure, 1 rue Maurice Arnoux, F-92120 Montrouge, France

Joseph Delhalle
Laboratoire de Chimie Théorique Appliquée, Département de Chimie, Facultés Universitaires Notre-Dame de la Paix,
61 rue de Bruxelles, B-5000 Namur, Belgium

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Momentum-space equations of the restricted Hartree-Fock method for quasi-one-dimensional systems are obtained and analyzed in view of direct numerical determination of their solutions. Calculations on the basis of known results on the infinite linear chain of hydrogen atoms whose Bloch states are approximated in terms of $1s$ hydrogenic atomic functions are made to test the formalism as well as the mathematical and computational implications of a numerical approach. Future developments along these lines are discussed on the basis of the practical knowledge imparted by these preliminary tests.

I. INTRODUCTION

Hartree-Fock (HF) equations and their solutions play a central role in the determination of the electronic structure of atoms, molecules, and extended systems [one-, two-, and three-dimensional (1D, 2D, and 3D)]. Unfortunately, exact solutions to the HF equations are not accessible in explicit forms, and as a consequence, applications on realistic systems are carried out with the one-electron states expanded in finite series of basis functions, usually of atomic character [linear combination of atomic orbitals (LCAO) approximation]. The error resulting from the truncation of the otherwise ideally infinite series is difficult to estimate. Moreover, its incidence largely depends upon the nature of the properties. Total energy and one-electron eigenvalues converge faster to their HF limit with respect to basis-set increases than other expectation values, such as the dipole moment, the electric field gradient, etc., which are rather sensitive to the details of the state functions and thus to basis-set extensions. In solid-state physics, this problem of choice of the most appropriate representations for the Bloch states has led to fierce controversies on the relative merits of delocalized [plane waves (PW), orthogonalized plane waves (OPW), etc.] and localized [tight-binding approximation (TBA), LCAO, etc.] functions.

Rather recently, Davis and co-workers[1-3] studied the possibility of improving the description of the Hartree-Fock states by building into the basis functions some analytical information inherent in the HF orbitals. They found that such attempts do not lead to better basis functions and they were forced to the conclusion that the problem of basis-set incompleteness cannot be solved by searching for new types of basis functions.[3] They also ruled out the traditional practice of enlarging basis sets due to prohibitive computer time and linear dependencies. Finally, they expressed their preference for approaches that do not rely on basis sets.

In the case of atoms[4] and diatomic molecules,[5-7] it is possible to achieve enough separability among the direct-space variables to solve the HF equations by numerical integration. These calculations have evidenced the fact that many functions must actually be used to eliminate the basis dependence from the results. For medium-sized systems, an equivalent level of quality cannot be reached by the algebraic or basis-set approach due to prohibitive computational needs. The numerical approach in direct-space is unfortunately not applicable to systems whose structural complexity exceeds two nuclei and no progress seems presently possible in this direction.

In 1981, Navaza and Tsoucaris[8] suggested that momentum (reciprocal) space should be a more appropriate framework to solve directly the HF equations for polyatomic systems. Two years later, Defranceschi *et al.*[9] were able to develop and apply the method to determine numerically in momentum space, the occupied molecular orbitals of the triatomic H_3 molecule. As we recently pointed out in a short communication,[10] there is nothing in the method that prevents it from being applicable to infinite systems. It is the purpose of the present paper to gain a first experience on the theoretical and practical problems related to direct numerical solutions of the HF equations for extended chain systems.

In Sec. II we obtain the general expressions of the momentum-space representation of the restricted Hartree-Fock (RHF) equations (i.e., restricted to the double occupancy of the Bloch states of lowest energy eigenvalues) for quasi-1D systems. A broad identification of the numerical and computational aspects inherent in these equations is made in Sec. III. In Sec. IV we report on our first attempts to apply a full numerical treatment to the integral part of these equations. The model system chosen is the infinite chain of hydrogen atoms whose approximate one-electron states are expressed as a Bloch sum based on one hydrogenic $1s$ functions successively expanded in one, two, and three spherical Gaussians. In the final section we comment on the future of the method and indicate directions for solving some of the already identified problems.

II. MOMENTUM-SPACE REPRESENTATION OF THE RHF EQUATIONS

The Fourier-representation method developed by Harris and co-workers[11–15] to calculate explicitly the matrix elements of the LCAO version of the RHF equations (RHF-LCAO) for extended systems, and the work by Navaza and Tsoucaris[8] and Defranceschi *et al.*[9] on molecules form the basic material from which we start. To facilitate access to these works we have largely maintained their notation and structure. A summary of the more familiar direct-space version of the RHF equations is given in Sec. II A; their momentum-space formulation is developed in Sec. II B.

A. The RHF equations in direct-space (Refs. 16–19)

First-principle quantum-mechanical calculations of the electronic structure of quasi-1D systems have almost exclusively been concerned with isolated regular model chains whose atomic positions can generally be obtained through line-group symmetry operations.[20] For the sake of convenience, but without loss in generality, only the translational symmetry is explicitly dealt with in this work. Within that framework, a quasi-1D system consists of a macroscopic number $N(\rightarrow\infty)$ of unit cells of length a_0 in the direction of periodicity defined by the unit vector $\mathbf{e}_z$. Each cell contains Ω nuclei at positions $\mathbf{s}_1, \mathbf{s}_2, \ldots, \mathbf{s}_u, \ldots, \mathbf{s}_\Omega$ relative to the cell origin $\mu a_0 \mathbf{e}_z$ $(\mu=0,\pm1,\pm2,\ldots)$, and ω electrons distributed along the nuclear framework. It is practical to have the position vectors $\mathbf{s}_u$ expressed in units of a_0. For the chain to be stable, the cell electroneutrality has to be fulfilled, i.e., $\omega=\sum_u Z_u$ with Z_u as the atomic number of atom u. The set of indices $(u,u'=1,2,\ldots,\Omega)$ and $(\mu,\mu',\nu,\nu'=0,\pm1,\pm2,\ldots)$ will refer, respectively, to the nuclei and the points of a lattice unit length.

In atomic units, the direct-space representation of the Hamiltonian of the model system (nuclear motion, magnetic and relativistic effects excluded) is

$$H=\sum_{i=1}^{\omega N}\left[-\tfrac{1}{2}\nabla^2(\mathbf{r}_i)+V(\mathbf{r}_i)\right] + \sum_{\substack{i,j=1\\ i<j}}^{\omega N} |\mathbf{r}_i-\mathbf{r}_j|^{-1}+U_N\,, \tag{1}$$

with $\mathbf{r}_i$ the position vector of electron i measured from an arbitrary but fixed origin, $V(\mathbf{r}_i)$ the nuclear attraction operator,

$$V(\mathbf{r}_i)=-\sum_{u=1}^{\Omega} Z_u \sum_{\mu} |\mathbf{r}_i-(\mathbf{s}_u+\mu\mathbf{e}_z)a_0|^{-1}\,, \tag{2}$$

and U_N the nuclear repulsion energy,

$$U_N=\tfrac{1}{2}\sum_{\mu,\mu'}\sum_{u,u'}{}'' Z_u Z_{u'} |[\mathbf{s}_u-\mathbf{s}_{u'}+(\mu-\mu')\mathbf{e}_z]a_0|^{-1} \tag{3a}$$

$$=\frac{N}{2}\sum_{\mu}\sum_{u,u'}{}'' Z_u Z_{u'} |(\mathbf{s}_u-\mathbf{s}_{u'}+\mu\mathbf{e}_z)a_0|^{-1}\,. \tag{3b}$$

In Eq. (3a) the double prime indicates omission of the term $\mu=\mu'$ [$\mu=0$ in Eq. (3b)] when $u=u'$. Unless otherwise indicated, all summations will be over the entire range for which the summed indices are defined.

The Hamiltonian will be applied to single-determinant wave functions built from doubly occupied RHF one-electron (single-particle) Bloch orbitals (states) $|k_n\rangle$ or $\phi_n(k,\mathbf{r})$ which can generally be written as

$$|k_n\rangle=\phi_n(k,\mathbf{r})=e^{2i\pi a_0^{-1}kz}u_n(k,\mathbf{r})\,, \tag{4}$$

where $u_n(k,\mathbf{r})$ is a function having the lattice periodicity; $k\,(k')$ and $n\,(n')=1,2,\ldots,\infty$, are respectively, the Bloch wave number and band index. In our notation, k is in units of $2\pi a_0^{-1}$, the Brillouin zone (BZ) corresponds to a unit range of k, i.e., $k\in[-\tfrac{1}{2},\tfrac{1}{2}]$ and a sum over k becomes, in the limit $N\rightarrow\infty$, $N\int dk$. By virtue of the phase factor of unit modulus appearing in Eq. (4), the Bloch functions $|k_n\rangle$ are orthogonal in k. Furthermore, it is convenient to require orthogonality in n as well as the normalization implied by

$$\langle k_n | k_{n'}\rangle = N\delta_{nn'}\,. \tag{5}$$

Applying the Hartree-Fock condition of minimum expectation value for the total energy E_N of the many-electron wave function subject to the above normalization conditions,

$$E_N=NE=N\left[\int_{\mathrm{BZ}}dk\sum_n\frac{\langle k_n|-\frac{1}{2}\nabla^2|k_n\rangle}{\langle k_n|k_n\rangle}+U+N\int_{\mathrm{BZ}}dk\int_{\mathrm{BZ}}dk'\sum_{n,n'}\frac{\langle k_n k'_{n'}|k_n k'_{n'}\rangle-\frac{1}{2}\langle k_n k'_{n'}|k'_{n'}k_n\rangle}{\langle k_n|k_n\rangle\langle k'_{n'}|k'_{n'}\rangle}\right], \tag{6}$$

yields the RHF equations. In Eq. (6), $U=N^{-1}U_N$. The explicit form of the $u_n(k,\mathbf{r})$ are determined by solving RHF equations, i.e.,

$$F(\mathbf{r})\phi_n(k,\mathbf{r})=\left[-\tfrac{1}{2}\nabla^2(\mathbf{r})-\sum_{\mu=-\infty}^{\infty}\sum_{u=1}^{\Omega}Z_u|\mathbf{r}-(\mathbf{s}_u+\mu\mathbf{e}_z)a_0|^{-1} + \sum_{n'}\int dk'\,\theta_{n'}(k')[J_{n'k'}(\mathbf{r})-\tfrac{1}{2}K_{n'k'}(\mathbf{r})]\right]\phi_n(k,\mathbf{r})=\varepsilon_n(k)\phi_n(k,\mathbf{r})\,. \tag{7}$$

The operators $J_{n'k'}(\mathbf{r})$ and $K_{n'k'}(\mathbf{r})$, respectively describing the classical electrostatic and exchange interactions, are expressed as

$$J_{n'k'}(\mathbf{r})\phi_n(k,\mathbf{r})=\left[\int d\mathbf{r}\,\phi^*_{n'}(k',\mathbf{r}')\,|\mathbf{r}-\mathbf{r}'|^{-1}\phi_{n'}(k',\mathbf{r})\right]\phi_n(k,\mathbf{r}) \tag{8a}$$

and

$$K_{n'k'}(\mathbf{r})\phi_n(k,\mathbf{r})=\left[\int d\mathbf{r}'\phi^*_{n'}(k',\mathbf{r}')\,|\mathbf{r}-\mathbf{r}'|^{-1}\phi_n(k,\mathbf{r}')\right]\phi_{n'}(k',\mathbf{r}), \tag{8b}$$

where $\varepsilon_n(k)$ is the single-particle energy of band n at point k in BZ, and $\theta_n(k)$ is the single-particle state occupation function [$\theta_n(k)=2$ when $|\,k_n\rangle$ is populated and $\theta_n(k)=0$ when $|\,k_n\rangle$ is unoccupied].

B. Momentum-space representation of the RHF equations

Applying a Fourier transformation to the direct-space RHF equations yields the corresponding expressions in momentum space. The various steps leading to the final equations are based on properties of the Fourier transform defined here as[15]

$$[f(\mathbf{r})]^T(\mathbf{q})=f^T(\mathbf{q})=\int d\mathbf{r}\,f(\mathbf{r})e^{2i\pi a_0^{-1}\mathbf{q}\cdot\mathbf{r}}, \tag{9}$$

so that the transform variable $\mathbf{q}$ is dimensionless and scaled like the Bloch wave number k. The most useful relations for our purposes are listed hereafter in a notation consistent with the definition in Eq. (9):

$$[-\tfrac{1}{2}\nabla^2 f(\mathbf{r})]^T(\mathbf{q})=\tfrac{1}{2}(2\pi a_0^{-1})^2q^2f^T(\mathbf{q}), \tag{10a}$$

$$[f(\mathbf{r})g(\mathbf{r}-\mathbf{R})]^T(\mathbf{q})$$
$$=a_0^{-3}\int d\mathbf{p}\,f^T(\mathbf{p})g^T(\mathbf{q}-\mathbf{p})e^{2i\pi a_0^{-1}(\mathbf{q}-\mathbf{p})\cdot\mathbf{R}}, \tag{10b}$$

$$|\,\mathbf{r}-\mathbf{R}\,|^{-1}=(\pi a_0)^{-1}\int\frac{d\mathbf{q}}{q^2}e^{-2i\pi a_0^{-1}\mathbf{q}\cdot(\mathbf{r}-\mathbf{R})}, \tag{10c}$$

$$\sum_\nu e^{2i\pi\nu q_z}=\sum_\nu\delta(q_z-\nu)\ . \tag{10d}$$

We first discuss the form of the Bloch orbitals in momentum space, and since many of the forthcoming results are expressible in terms of the Fourier transforms over products of Bloch orbitals, we also introduce their definition before considering the RHF equations themselves.

1. *Bloch orbitals in momentum space*

Applying the Fourier transform defined in Eq. (9) to the direct-space form of the Bloch states lead to the corresponding expression in momentum space:

$$\phi_n^T(k,\mathbf{p})=\int d\mathbf{r}\,e^{2i\pi a_0^{-1}\mathbf{p}\cdot\mathbf{r}}\phi_n(k,\mathbf{r})$$
$$=\int d\mathbf{r}\,e^{2i\pi a_0^{-1}\mathbf{p}\cdot\mathbf{r}}e^{2i\pi a_0^{-1}kz}u_n(k,\mathbf{r})\ . \tag{11}$$

The above expression can be further specified if $u_n(k,\mathbf{r})$, which has the translational periodicity of the lattice in direct space, is expanded in a Fourier series,

$$u_n(k,\mathbf{r})=a_0^{-1}\sum_\nu\tilde{u}_n(k,\mathbf{r}_\perp;\nu)e^{-2i\pi a_0^{-1}\nu z},\quad \mathbf{r}_\perp\equiv(x,y) \tag{12}$$

with $\tilde{u}_n(k,\mathbf{r}_\perp;\nu)$ as the νth Fourier coefficient obtained from the usual prescription,

$$\tilde{u}_n(k,\mathbf{r}_\perp;\nu)=\int_{z_0}^{z_0+a_0}dz\,u_n(k,\mathbf{r})e^{2i\pi a_0^{-1}\nu z} \tag{13}$$

and z_0 an arbitrary point on the axis of translational periodicity. Inserting Eq. (12) in Eq. (11), using the following definition for $u_n^T(k,\mathbf{p}_\nu)$,

$$u_n^T(k,\mathbf{p}_\nu)=\int d\mathbf{r}_\perp\,e^{2i\pi a_0^{-1}\mathbf{p}_\perp\cdot\mathbf{r}_\perp}\tilde{u}_n(k,\mathbf{r}_\perp;\nu), \tag{14}$$

and denoting $\mathbf{p}_\perp=(p_x,p_y)$ and $\mathbf{p}_\nu=(p_x,p_y,\nu)$, yields

$$\phi_n^T(k,\mathbf{p})=a_0^{-1}\sum_\nu\int dz\,e^{2i\pi a_0^{-1}z[p_z-(\nu-k)]}$$
$$\times\int d\mathbf{r}_\perp\,e^{2i\pi a_0^{-1}\mathbf{p}_\perp\cdot\mathbf{r}_\perp}u_n(k,\mathbf{r})$$
$$=\sum_\nu\delta[p_z-(\nu-k)]u_n^T(k,\mathbf{p}_\nu)\ . \tag{15}$$

It is worth stressing that, while $\phi_n(k,\mathbf{r})$ is a continuous function of x,y,z, its momentum transform $\phi_n^T(k,\mathbf{p})$ is a continuous function of p_x and p_y only and a discrete function of the third variable p_z. The discrete part can be represented by a set of equally spaced δ functions having the weight $u_n^T(k,\mathbf{p})$ ar $p_z=\nu-k$ ($\nu=0,\pm1,\pm2,\dots$) and thus identifies with a Dirac comb.

2. *Fourier transform of orbital products $W_{nn'}(k,k',\mathbf{q})$*

As will soon become apparent, the Fourier transform over products of Bloch orbitals $W_{nn'}(k,k',\mathbf{q})$ are central quantities and are thus ideally defined at this point,

$$W_{nn'}(k,k',\mathbf{q})=\int d\mathbf{r}\,\phi_n^*(k,\mathbf{r})\phi_{n'}(k',\mathbf{r})e^{2i\pi a_0^{-1}\mathbf{q}\cdot\mathbf{r}}\ . \tag{16}$$

Using the property in Eq. (10b) leads to the following expression:

$$W_{nn'}(k,k',\mathbf{q})=a_0^{-3}\int d\mathbf{s}\,\phi_n^{T*}(k,\mathbf{s}-\mathbf{q})\phi_{n'}^T(k',\mathbf{s}), \tag{17}$$

which, after insertion of the momentum-space representation of the Bloch state in the form given by Eq. (15), becomes

$$W_{nn'}(k,k',\mathbf{q})=a_0^{-3}\sum_{\nu,\nu'}\int d\mathbf{s}\,\delta(s_z-q_z-(\nu-k))\delta(s_z-(\nu'-k'))u_n^{T*}(k,\mathbf{s}_\perp-\mathbf{q}_\perp,\nu)u_{n'}^T(k',\mathbf{s}_\perp,\nu')$$
$$=a_0^{-3}\sum_{\nu,\nu'}\int ds_z\,\delta(s_z-(q_z+\nu-k))\delta(s_z-(\nu'-k'))\int d\mathbf{s}_\perp\,u_n^{T*}(k,\mathbf{s}_\perp-\mathbf{q}_\perp,\nu)u_{n'}^T(k',\mathbf{s}_\perp,\nu')\ . \tag{18}$$

Using the following identity,

$$\int ds\,\delta(s_z-a)\delta(s_z-b)=\delta(a-b)\,, \tag{19}$$

and replacing $\nu'-\nu$ and ν' by μ and ν, respectively, gives

$$\begin{aligned} W_{nn'}(k,k',\mathbf{q})&=a_0^{-3}\sum_{\nu,\nu'}\delta(q_z-[(\nu'-\nu)-(k-k')])\int d\mathbf{s}_\perp\, u_n^{T*}(k,\mathbf{s}_\perp-\mathbf{q}_\perp,\nu)u_{n'}^T(k',\mathbf{s}_\perp,\nu') \\ &=a_0^{-3}\sum_\mu \delta(q_z-(\mu+k'-k))\int d\mathbf{s}_\perp\sum_\nu u_n^{T*}(k,\mathbf{s}_\nu-\mathbf{q}_\mu)u_{n'}^T(k',\mathbf{s}_\nu)\,. \end{aligned} \tag{20}$$

To compress some of the expressions, it is practical to introduce the auxiliary quantity, $W_{nn'}(k,k',\mathbf{q}_{\mu+k-k'})$, defined as

$$W_{nn'}(k,k',\mathbf{q}_{\mu+k-k'})=a_0^{-3}\delta(q_z-(\mu+k-k'))\int d\mathbf{s}_\perp\sum_\nu u_n^{T*}(k,\mathbf{s}_\nu-\mathbf{q}_\mu)u_{n'}^T(k',\mathbf{s}_\nu)\,, \tag{21}$$

so that

$$W_{nn'}(k,k',\mathbf{q})=\sum_\mu W_{nn'}(k,k',\mathbf{q}_{\mu+k-k'})\,. \tag{22}$$

$W_{nn'}(k,k',\mathbf{q})$ is a continuous function of p_x and p_y only and a Dirac comb of the third variable p_z as is $\phi_n^T(k,\mathbf{p})$.

3. *Momentum representation of the RHF equations*

The RHF equations expressed in momentum space are obtained after applying a Fourier transform to the direct-space formulation of that equation, Eq. (7):

$$\begin{aligned} [F(\mathbf{r})\phi_n(k,\mathbf{r})]^T(\mathbf{p})&=\varepsilon_n(k)[\phi_n(k,\mathbf{r})]^T(\mathbf{p}) \\ &=\varepsilon_n(k)\phi_n^T(k,\mathbf{p})\,. \end{aligned} \tag{23}$$

The linearity of the Fourier transformation permits an individual treatment for the terms constituting $F(\mathbf{r})$, namely the kinetic-energy term, the classical electron-electron and electron-nuclear terms, and the exchange contribution.

a. Kinetic-energy term. Using Eq. (10a) the kinetic-energy part of the Fock operator is easy to express in momentum space,

$$[-\tfrac{1}{2}\nabla^2(\mathbf{r})\phi_n(k,\mathbf{r})]^T(\mathbf{p})=\tfrac{1}{2}(2\pi a_0^{-1})^2p^2\phi_n^T(k,\mathbf{p})=\tfrac{1}{2}(2\pi a_0^{-1})^2\sum_\nu\delta(p_z-(\nu-k))p^2u_n^T(k,\mathbf{p}_\nu)\,. \tag{24}$$

b. Electrostatic terms. Electron-electron and electron-nuclear terms in Eq. (7) contain divergent series related to the long-range nature of the Coulomb force. In the case of electrically neutral systems, the divergencies can be made to cancel by combining the individually divergent terms. The resulting series is conditionally convergent, but an unambiguous result is obtained upon imposing the physical condition that the partial sums represent neutral samples. The sum of the electron-electron and electron-nuclear terms contributed by band n and denoted $C_n(k,\mathbf{r})$ is

$$C_n(k,\mathbf{r})=\left[\sum_{n'}\int_{\mathrm{BZ}}dk'\,\theta_{n'}(k')\left[\int d\mathbf{r}'\,\phi_{n'}^*(k',\mathbf{r})\,|\mathbf{r}-\mathbf{r}'|^{-1}\phi_{n'}(k',\mathbf{r}')\right]-\sum_\mu\sum_u Z_u\,|\mathbf{r}-(\mathbf{s}_u+\mu\mathbf{e}_z)a_0|^{-1}\right]\phi_n(k,\mathbf{r})\,. \tag{25}$$

Inserting the Fourier representation of $|\mathbf{r}-\mathbf{r}'|^{-1}$ and $|\mathbf{r}-(\mathbf{s}_u+\mu\mathbf{e}_z)a_0|^{-1}$, see Eq. (10c), and applying the Fourier transform to Eq. (24) gives

$$\begin{aligned} [C(k,\mathbf{r})]_n^T(\mathbf{p})=C_n^T(k,\mathbf{p})&=(\pi a_0)^{-1}\int d\mathbf{r}\,e^{2i\pi a_0^{-1}\mathbf{p}\cdot\mathbf{r}}\left[\sum_{n'}\int dk'\,\theta_{n'}(k')\int d\mathbf{r}'\,\phi_{n'}^*(k',\mathbf{r}')\phi_{n'}(k',\mathbf{r})\int\frac{d\mathbf{q}}{q^2}e^{-2i\pi a_0^{-1}\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}\right. \\ &\qquad\left.-\sum_\mu\sum_u Z_u\int\frac{d\mathbf{q}}{q^2}e^{-2i\pi a_0^{-1}\mathbf{q}\cdot(\mathbf{r}-\mathbf{s}_ua_0)}e^{2i\pi\mu q_z}\right]\phi_n(k,\mathbf{r}) \\ &=(\pi a_0)^{-1}\int\frac{d\mathbf{q}}{q^2}\left[\sum_{n'}\int dk'\,\theta_{n'}(k')W_{n'n'}(k',k',\mathbf{q})-\sum_\mu\sum_u Z_u e^{2i\pi(\mathbf{q}\cdot\mathbf{s}_u+\mu q_z)}\right]\phi_n^T(k,\mathbf{p}-\mathbf{q})\,. \end{aligned} \tag{26}$$

Introducing the explicit form of $W_{n'n'}(k',k',\mathbf{q})$, Eq. (20), in the above expression gives

$$\begin{aligned} C_n^T(k,\mathbf{p})&=(\pi a_0)^{-1}\int\frac{d\mathbf{q}}{q^2}\left[\sum_{n'}\int dk'\,\theta_{n'}(k')a_0^{-3}\sum_\mu\delta(q_z-\mu)\int d\mathbf{s}_\perp\sum_\nu u_{n'}^{T*}(k',\mathbf{s}_\nu-\mathbf{q}_\mu)u_n^T(k',\mathbf{s}_\nu)\right. \\ &\qquad\left.-\sum_\mu\sum_u Z_u e^{2i\pi(\mathbf{q}\cdot\mathbf{s}_u+\mu q_z)}\right]\phi_n^T(k,\mathbf{p}-\mathbf{q}) \\ &=(\pi a_0)^{-1}\int\frac{d\mathbf{q}}{q^2}\sum_\mu\delta(q_z-\mu)\left[\sum_{n'}\int dk'\,\theta_{n'}(k')W_{n'n'}(k',k',\mathbf{q}_\mu)-\sum_u Z_u e^{2i\pi\mathbf{q}\cdot\mathbf{s}_\mu}\right]\phi_n^T(k,\mathbf{p}-\mathbf{q})\,, \end{aligned} \tag{27}$$

where Eqs. (10d) and (21) have been applied.

At this point, it is important to note that at $\mathbf{q}=0$ both the electron-electron and electron-nuclear terms diverge. However, due to the electroneutrality condition, these terms are equal in magnitude and opposite in sign, and therefore cancel exactly at $\mathbf{q}=0$,

$$a_0^{-3}\sum_{n'}\int dk'\,\theta_{n'}(k')\int d\mathbf{s}_\perp \sum_{\nu} u_{n'}^{T^*}(k',\mathbf{s}_\nu)u_{n'}^{T}(k',\mathbf{s}_\nu)=\omega=\sum_u Z_u\,, \tag{28}$$

which removes the problematic singularity. Harris[13] has shown that interchanging the q integration and the μ summation is permitted; therefore, Eq. (27) becomes

$$C_n^T(k,\mathbf{p})=(\pi a_0)^{-1}\sum_\mu \int \frac{d\mathbf{q}_\perp}{q_\perp^2+\mu^2}\left[\sum_{n'} dk'\,\theta_{n'}(k')W_{n'n'}(k',k',\mathbf{q}_\mu)-\sum_u Z_u e^{2i\pi\mathbf{q}_\mu\cdot\mathbf{s}_u}\right]\phi_n^T(k,\mathbf{p}-\mathbf{q}_\mu)\,. \tag{29}$$

Due to cancellations between electron-electron and electron-nuclear terms, the integral in Eq. (19) is of bounded value. In the vicinity of $\mathbf{q}=0$ ($\mathbf{q}_\perp=\mathbf{0},\mu=0$), the singularity has been weakened and integrations in arbitrarily small regions around this point yield finite contributions. At large values of $|\mathbf{q}|$ the multiplicative function $\phi_n^T(k,\mathbf{p}-\mathbf{q}_\mu)$ provides the necessary decay for $C_n^T(k,\mathbf{p})$ to be finite. The asymptotic decay of $\phi_n^T(k,\mathbf{q})$ results from the Coulombic nature of the interactions involved in the potential term of the Hamiltonian. In direct space, the wave functions must decay like exponentials at large $|\mathbf{r}|$ and in momentum space the characteristic decay will be of the form $\sim|\mathbf{q}|^{-\upsilon}$ ($\upsilon>0$) as, for example, in the case of the $1s$ hydrogenic wave function where $\upsilon=4$.

c. Exchange terms. The direct-space representation of the exchange part, $X_n(k,\mathbf{r})$, due to band n,

$$X_n(k,\mathbf{r})=-\tfrac{1}{2}\sum_{n'}\int dk'\,\theta_{n'}(k')\left[\int d\mathbf{r}'\,\phi_{n'}^*(k',\mathbf{r}')\,|\mathbf{r}-\mathbf{r}'|^{-1}\phi_n(k,\mathbf{r}')\right]\phi_n'(k',\mathbf{r})\,, \tag{30}$$

can be expressed in the momentum-space representation by following the same steps as in the case of the electrostatic terms,

$$\begin{aligned}X_n^T(k,\mathbf{p})&=-(2\pi a_0)^{-1}\int\frac{d\mathbf{q}}{q^2}\sum_{n'}\int dk'\,\theta_{n'}(k')\int d\mathbf{r}'\,\phi_{n'}^*(k',\mathbf{r}')\phi_n(k,\mathbf{r}')e^{2i\pi a_0^{-1}\mathbf{q}\cdot\mathbf{r}'}\int d\mathbf{r}\,e^{2i\pi a_0^{-1}(\mathbf{p}-\mathbf{q})\cdot\mathbf{r}}\phi_{n'}(k',\mathbf{r})\\&=-(2\pi a_0)^{-1}\int\frac{d\mathbf{q}}{q^2}W_{n'n}(k',k,\mathbf{q})\phi_{n'}^T(k',\mathbf{p}-\mathbf{q})\,.\end{aligned} \tag{31}$$

Replacing $W_{n'n}(k',k,\mathbf{q})$ by the explicit form in Eq. (21), leads to

$$\begin{aligned}X_n^T(k,\mathbf{p})&=-(2\pi a_0)^{-1}\int\frac{d\mathbf{q}}{q^2}\sum_{n'}\int dk'\,\theta_{n'}(k')\sum_\mu\delta[q_z-(\mu+k'-k)]\\&\qquad\times\int d\mathbf{s}_\perp\sum_\nu u_{n'}^{T^*}(k',\mathbf{s}_\nu-\mathbf{q}_\mu)u_n^T(k,\mathbf{s}_\nu)\phi_{n'}^T(k',\mathbf{p}-\mathbf{q})\\&=-(2\pi a_0)^{-1}\sum_\mu\int dk'\int\frac{d\mathbf{q}_\perp}{q_\perp^2+(\mu+k'-k)^2}\sum_{n'}\theta_{n'}(k')W_{n'n}(k',k,\mathbf{q}_{\mu+k'-k})\phi_{n'}^T(k',\mathbf{p}-\mathbf{q}_{u+k'-k})\,.\end{aligned} \tag{32}$$

Contrary to the case of electrostatic contributions, unremovable singularities occur at $q_\perp^2+(\mu+k'-k)^2=0$ (i.e., $\mathbf{q}_\perp=0$; $\mu=0$ with $k=k'$, $\mu=1$ with $k=-k'=-\frac{1}{2}$, and $\mu=-1$ with $-k=k'=\frac{1}{2}$). Nevertheless, the contributions originating from the regions of singularity accumulate to a finite result after integration over $q_\perp$ and k'. However, as was already experienced in the algebraic approach,[15] this causes many problems in performing the numerical integrations. This will be mentioned in the next section with emphasis on the fully numerical approach. The behavior of the integrand at large values of $|\mathbf{q}|$ follows the same trends as in the case of the electrostatic terms.

d. Total energy. An appropriate form of the total energy for our computational purposes is

$$E_N=\frac{N}{2}\int_{\mathrm{BZ}}dk\sum_n\{\theta_n(k)[\varepsilon_n(k)+T_n(k)+V_n(k)]\}+U_N\,, \tag{33}$$

where

$$\begin{aligned}\varepsilon_n(k)&=\int d\mathbf{r}\,\phi_n^*(k,\mathbf{r})F(\mathbf{r})\phi_n(k,\mathbf{r})\\&=a_0^{-3}\int d\mathbf{p}\,\phi_n^{T^*}(k,\mathbf{p})[F(\mathbf{r})\phi_n(k,\mathbf{r})]^T(\mathbf{p})\,,\end{aligned} \tag{34}$$

$$\begin{aligned}T_n(k)&=\int d\mathbf{r}\,\phi_n^*(k,\mathbf{r})[-\tfrac{1}{2}\nabla^2(\mathbf{r})]\phi_n(k,\mathbf{r})\\&=a_0^{-3}\int d\mathbf{p}\,\phi_n^{T^*}(k,\mathbf{p})[-\tfrac{1}{2}\nabla^2(\mathbf{r})\phi_n(k,\mathbf{r})]^T(\mathbf{p})\,,\end{aligned} \tag{35}$$

$$\begin{aligned}V_n(k)&=\int d\mathbf{r}\,\phi_n^*(k,\mathbf{r})\phi_n(k,\mathbf{r})\\&\qquad\times\left[-\sum_\mu\sum_u Z_u\,|\mathbf{r}-(\mathbf{s}_u+\mu\mathbf{e}_z)a_0|^{-1}\right],\end{aligned} \tag{36}$$

and

$$U_N=\frac{N}{2}\sum_\mu\sum_{u,u'}{}''\,Z_uZ_{u'}\,|(\mathbf{s}_u-\mathbf{s}_{u'}+\mu\mathbf{e}_z)a_0|^{-1}=NU\,, \tag{37}$$

with $U=N^{-1}U$. It is possible to factorize out N, the number of cells, and to write the total energy per unit cell E as

$$E=\tfrac{1}{2}\int_{\mathrm{BZ}} dk \sum_n \theta_n(k)[\varepsilon_n(k)+T_n(k)]+U+V\,, \tag{38}$$

V being defined as

$$V=\tfrac{1}{2}\int_{\mathrm{BZ}} dk \sum_n \theta_n(k)V_n(k)\,. \tag{39}$$

In Eq. (38) both U and V are individually divergent terms, the divergence is resolved through a grouping similar to the one applied to the electrostatic terms occurring in $F(\mathbf{r})$.

We proceed by writing U in a Fourier-representation form; using Eq. (10c), we obtain

$$\begin{aligned}U&=\tfrac{1}{2}\sum_\mu\sum_u Z_u \sum_{u'}{}'' Z_{u'}\,|(\mathbf{s}_u-\mathbf{s}_{u'}+\mu\mathbf{e}_z)a_0|^{-1}=(2\pi a_0)^{-1}\sum_u Z_u\sum_\mu\sum_{u'}{}'' Z_{u'}\int\frac{d\mathbf{q}}{q^2}e^{-2i\pi\mathbf{q}\cdot(\mathbf{s}_u-\mathbf{s}_{u'}+\mu\mathbf{e}_z)}\\&=(2\pi a_0)^{-1}\sum_u Z_u\left[\sum_{u'}Z_{u'}\sum_\mu\int\frac{d\mathbf{q}}{q^2}e^{-2i\pi\mathbf{q}\cdot(\mathbf{s}_u-\mathbf{s}_{u'}+\mu\mathbf{e}_z)}-Z_\mu\int\frac{d\mathbf{q}}{q^2}\right].\end{aligned} \tag{40}$$

In the last line of Eq. (40), the term $\mu=0$, $u=u'$, initially excluded by the double-prime convention, has been added and subtracted. The term V is treated in a similar way, i.e.,

$$\begin{aligned}V&=\tfrac{1}{2}\int dk\sum_n\theta_n(k)\int d\mathbf{r}\,\phi_n^*(k,\mathbf{r})\phi_n(k,\mathbf{r})\left[-\sum_\mu\sum_u Z_u\,|\mathbf{r}-(\mathbf{s}_u+\mu\mathbf{e}_z)a_0|^{-1}\right]\\&=(2\pi a_0)^{-1}\int dk\sum_n\theta_n(k)\int d\mathbf{r}\,\phi_n^*(k,\mathbf{r})\phi_n(k,\mathbf{r})\left[-\sum_\mu\sum_u Z_u\int\frac{d\mathbf{q}}{q^2}e^{2i\pi a_0^{-1}\mathbf{q}\cdot[\mathbf{r}-(\mathbf{s}_u+\mu\mathbf{e}_z)a_0]}\right]\\&=(2\pi a_0)^{-1}\int dk\sum_n\theta_n(k)\left[-\sum_\mu\sum_u Z_u\int\frac{d\mathbf{q}}{q^2}W_{nn}(k,k,\mathbf{q})e^{-2i\pi\mathbf{q}\cdot(\mathbf{s}_u+\mu\mathbf{e}_z)}\right].\end{aligned} \tag{41}$$

We now combine U and V, interchange the μ summation and the $\mathbf{q}$ integration, insert Eq. (10d) and integrate over q_z to obtain

$$U+V=(2\pi a_0)^{-1}\sum_u Z_u\int d\mathbf{q}_\perp\left[\sum_\mu\frac{e^{-2i\pi\mathbf{q}_\mu\cdot\mathbf{s}_u}}{q_\perp^2+\mu^2}\left[\sum_{u'}Z_{u'}e^{2i\pi\mathbf{q}_\mu\cdot\mathbf{s}_{u'}}-\int dk\sum_n\theta_n(k)W_{nn}(k,k\mathbf{q}_\mu)\right]-\frac{\pi Z_u}{|\mathbf{q}_\perp|}\right]. \tag{42}$$

As already pointed out in the algebraic approach,[12,13,15] Eq. (46) has a regular behavior not only at $\mathbf{q}_\mu=0$ but also at large $\mathbf{q}_\perp$. This can be made more obvious by separating from the u' summation the term $u'=u$ to finally obtain

$$\begin{aligned}U+V=(2\pi a_0)^{-1}\sum_u Z_u\int d\mathbf{q}_\perp\Bigg[&Z_u\Bigg[\sum_\mu\frac{1}{q_\perp^2+\mu^2}-\frac{\pi}{|\mathbf{q}_\perp|}-\frac{e^{-2i\pi\mathbf{q}_\perp\cdot\mathbf{s}_u}}{q_\perp^2}\int dk\sum_n\theta_n(k)W_{nn}(k,k,\mathbf{q}_\perp)\\&\qquad-\sum_{\mu\,(\neq 0)}\frac{e^{-2i\pi\mathbf{q}_\mu\cdot\mathbf{s}_u}}{q_\perp^2+\mu^2}\int dk\sum_n\theta_n(k)W_{nn}(k,k,\mathbf{q}_\mu)\Bigg]\\&+\sum_\mu\frac{e^{-2i\pi\mathbf{q}_\mu\cdot\mathbf{s}_u}}{\mathbf{q}_\perp^2+\mu^2}\Bigg[\sum_{\substack{u'\\u'\neq u}}Z_{u'}e^{2i\pi\mathbf{q}_\mu\cdot\mathbf{s}_{u'}}-\int dk\sum_n\theta_n(k)W_{nn}(k,k,\mathbf{q}_\mu)\Bigg]\Bigg].\end{aligned} \tag{43}$$

Equation (43) is well conditioned from a formal point of view,[12,13] but its numerical treatment requires to add and subtract analytical contributions in order to secure numerically accurate and stable results. Such procedures have been suggested by Harris[12] and have already been used in an application of the Fourier-representation method.[15]

The way in which difficulties related to these problems manifest in direct numerical integration of the RHF equations will only be understood and mastered from test calculations of gradually increasing complexity.

III. OVERVIEW OF THE COMPUTATIONAL ASPECTS

A full account of the computational and numerical features characteristic of the approach is neither possible nor appropriate at this stage of development. The computational strategy and procedures used in our preliminary calculations are likely to be adjusted according to the new knowledge the future computational experiments and tests will impart. Nevertheless, it is already informative to analyze the expressions established in Sec. II on the basis of their general and constant features.

An appreciable advantage of transforming to momentum space is that the RHF equations come out in the form of integral equations, while in direct space the corresponding expressions are of the integro-differential type. Integration is thus the basic operation that shall pervasively be performed to solve Eq. (23) numerically. The variables and the different types of integrations arising in the method are identified in Sec. III A. Sec. III B is devoted to a brief discussion of problems related to singular integrands.

A. Variables and integration schemes

The Bloch states, Eq. (15), and derived quantities such as a Fourier transform of orbital products, Eq. (22), depend upon four variables: the wave number k, two continuous coordinates p_x, p_y, and a discrete coordinate $p_z = \nu - k$. The continuous variables p_x and p_y as well as the index ν have double infinite ranges. It can already be anticipated that the tractability of a fully numerical treatment is closely linked to the actual decay of the relevant quantities, $\phi_n^T(k,\mathbf{p})$ and $W_{n,n'}(k,k',\mathbf{p})$, with respect to p. The more delocalized the functions and the more difficult will become the numerical work due to increasing storage requirements. The already identified singularities in some of the integrands suggest that we adopt a polar representation for the two continuous variables p_x and p_y, i.e., $(p_x,p_y) \rightarrow (\theta,p)$, which proves to be more convenient do deal with the expressions near the points of singularity. The range of θ and p, respectively, are $0 \leq \theta \leq \pi$ and $0 \leq p \leq \infty$. Translational symmetry decouples p_z from the other two variables, θ and p, and thereby implies a separate numerical treatment.

1. k integration

The process of populating the Bloch states of energy lower that the Fermi energy involves an integration over $k(k')$ in BZ [see, for instance, Eqs. (29), (32), and (43)]. In the case of our model system $(H)_x$, this type of integration has been performed using the standard Gauss-Legendre method,[21] and it was noticed that 6–10 points in half the Brillouin zone led to stable and consistent values.

2. (θ,p) integration

The region of integration for the p variable is a singly infinite interval, $0 \leq p \leq \infty$, and the corresponding integral is known as an improper integral. From preliminary attempts, it does not seem obvious that some sort of advantage can be gained by trading the unbounded interval for a finite one through a change of variable. One straightforward way to deal with such integral is to reduce the infinite interval by ignoring the tail of the integrands. However, in this case it is important to estimate the error resulting from such a truncation, and presently, we do not have simple and reliable inequalities from which to get error bounds for a given truncation. Nevertheless, the previous works on the molecular systems,[9,22] H_2 and H_3, have indicated that the relevant part of the one-electron states is enclosed in a disk $d(0,p_{\text{in}})$, hereafter referred to as the inner region, whose radius, p_{in}, is ≤ 3 a.u. of momentum. However, it was also observed that this was not sufficient to yield energetic quantities such as the total energy and one-electron eigenvalues more significant than within three decimal digits. To improve the situation an outer region, extending from p_{in} to p_{out}, was added. Typical values for p_{out} are 15 and 20 a.u. In the outer region simple analytical forms, deriving from the shape of the 1s hydrogenic wave function, were used to continue the numerical values from the inner region into the outer region and ease the computational work.

The integration method used in this paper for $d(0,p_{\text{in}})$ is an adaptation to the two-dimensional case of a procedure originally developed by Pierce[23] for spherical shells. The p abscissas are the nodes used in the standard Gauss-Legendre quadrature for a finite interval,[21] while the θ abscissas are evenly distributed on circles intersecting the radial axis at the p nodes. Computer tests on molecules[9,22] and in this work suggest that 27–37 p points per a.u. of momentum and 10–15 θ values are suitable grids to yield numerically accurate values to within four decimal digits.

3. μ summation

As a result of the lattice orthogonality relation, Eq. (10d), the integration over the variable $p_z = \mu - k$ reduces to an infinite summation of the functions defined at the points of a Dirac comb. The summation index runs in principles from $-\infty$ to $+\infty$. For localized functions in momentum space (delocalized functions in direct space), the series have a favorable rate of convergence. In the case of moderate and/or low convergence, procedures for summing the series become rapidly necessary but their use is subordinated to an explicit knowledge of the terms, which is obviously not the case in a numerical procedure. To overcome the difficult, the full range of the μ indices can be divided in an inner region, $-\mu_{\text{in}} \leq \mu \leq \mu_{\text{in}}$, where the terms of numerical origin are directly summed, and an external region where the remaining terms have the same explicit form as introduced for the p variable and can be summed by some analytical device.[13,24–26]

4. Interpolation

The occurrence of convolution integrals in the working expressions, see, e.g, Eq. (21), requires the knowledge of the state functions and other quantities for arguments not defined at grid points fixed by the numerical integration schemes. In such cases approximation procedures are needed. In the molecular applications and in this work these values are approximated by a cubic interpolation.[21]

B. Singular integrands

Extended systems generate problems of their own characterized by singularities in the integrands of both electrostatic, Eqs. (20) and (43), and exchange, (Eq. (32), contributions.

The divergencies arising from the singularities in the vicinity of $\mathbf{q}_\mu=0$ (or $q_x=q_y=\mu=0$) for integrands of Eqs. (29) and (43) have been removed by the combination of two terms equal in magnitude and opposite in sign, and does not hide new formal problems.[13,26] However, the evaluation of the integrals in Eqs. (29) and (43) remains difficult in practice because the terms $\mathbf{q}_\mu^2$ in the denominator enhance the numerical errors when $\mathbf{q}_\mu \to 0$. Mathematical manipulations such as adding and subtracting analytical forms[12] to reduce the ill-conditioned nature of the integrand at $\mathbf{q}_\mu \to 0$ are useful, especially in the case of total energy. This is alluded to in the following section.

Much more problematic is the exchange singularity which, contrary to the electrostatic situation, cannot be reduced on the basis of physical criteria. The integrand in Eq. (29) is unbounded when $\mathbf{q}_{\mu+k'-k} \to 0$, but the contributions originating from the regions of singularities are nevertheless finite as can be easily appreciated from the following simpler expression having the same singular behavior as in Eq. (32):

$$I=-(2\pi a_0)^{-1}\sum_\mu \int_c^d dk' \int_\sigma \frac{d\mathbf{q}_\perp}{\mathbf{q}_\perp^2+(\mu+k'-k)^2}$$

$$=-(2a_0)^{-1}\sum_\mu \int_c^d dk' \int_0^{p^2} \frac{ds}{s+(\mu+k'-k)^2}\,, \tag{44}$$

where $|c|$ and $|d| \le \frac{1}{2}$, and σ is a circular region of radius $\rho=[(q_x^2+q_y^2)]^{1/2}$ enclosing the origin. The above expression is the same as Eq. (32) where the numerator

$$\sum_{n'} \theta_{n'}(k')W_{nn'}(k',k,\mathbf{q}_{\mu+k'-k})\phi_{n'}^T(k',\mathbf{p}-\mathbf{q}_{\mu+k'-k})\,,$$

which does not contribute to the singularity, has been set to unity for the sake of illustration. Equation (44) can be given an explicit form since both q and k' integrations have a tabular entry:[27]

$$I=-(2a_0)^{-1}\sum_\mu \left[k'\ln\left[\frac{\rho^2+(k')^2}{(k')^2}\right] + 2\rho\tan\left[\frac{k'}{\rho}\right]\right]_{c+\mu-k}^{d+\mu-k}\,. \tag{45}$$

It is easily observed that Eq. (45) leads to a finite result no matter how small ρ is and whatever the integration limits for the k' integration chosen within the range of variation of k', i.e., $|k'| \le \frac{1}{2}$. This simple exercise shows that $X_n^T(k,\mathbf{p})$, Eq. (32), is bounded for any n, k, and $\mathbf{p}$ but, even more important than in the case of the electrostatic terms, the regions for which $\mathbf{q}_{\mu+k'-k} \to 0$ are ill conditioned and require special treatments. The way this problem has been dealt with for $(\mathrm{H})_x$ is described in the following section.

IV. APPLICATION TO THE $(\text{—H—})_x$ MODEL CHAIN

The infinite chain of hydrogen atoms, $(\mathrm{H})_x$, is the simplest quasi-1D system that can be conceived for meaningful *ab initio* test calculations. Its electronic structure has been investigated many times[15,28-33] and thus serves as a convenient reference for testing new approaches. Recently published data on this system by the algebraic Fourier representation method[15] and a direct-space approach[33] will be used to compare with our results.

In the model system, the hydrogen atoms are equally spaced. The basic parameters entering the preceding expressions are all equal to unity, $Z=\Omega=\omega=1$, and the one-electron states corresponding to the lowest-energy band $n=1$, are constructed from a single $1s$ hydrogenic function, denoted by χ, of exponent ζ. In order to simplify the notation, the subscript n has been removed from the expressions as suggested in Eq. (46). Since each hydrogen atom contributes one electron, in the double occupancy scheme, the occupation function $\theta_1(k)=\theta(k)$ is equal to 2 for $|k| \le \frac{1}{4}$ and zero elsewhere:

$$\phi_1(k,\mathbf{r})=\phi(k,\mathbf{r})=D_k\sum_\nu e^{2i\pi\nu k}\chi(\mathbf{r}-\nu a_0\mathbf{e}_z)\,. \tag{46}$$

Using the same method employed in Ref. 15, χ is approximated by a finite ($m=1,2,3$) Gaussian expansion,

$$\chi(\mathbf{r})=D_k\sum_{a=1}^m d_a\left[\frac{2\alpha_a}{\pi}\right]^{3/4} e^{-\alpha_a \mathbf{r}^2}\,. \tag{47}$$

The momentum-space version of Eq. (46) is

$$\phi^T(k,\mathbf{p})=D'_k\sum_\nu \delta(p_z-(\nu-k))\sum_{a=1}^m d_a\left[\frac{2\pi}{\alpha_a}\right]^{3/4} e^{-\beta_a\mathbf{p}^2}\,. \tag{48}$$

D_k and D'_k are normalization factors and $\beta_a=\pi^2(a_0^2\alpha_a)^{-1}$. The values of the parameters entering Eqs. (46) and (48) are listed in Table I. From Fig. 1 it can be noticed that $\phi^T(k,\mathbf{p})$ has more diffuse and more localized components when m increases. The actual values of the exponents and weights are listed in Table I. Equations (46) and (48) constitute approximate but fully defined expressions for the Bloch states of lowest-energy band once the parameters a_0 and ζ are fixed. In this work the variationally optimized[15] values of a_0 and ζ have been used, see Table I. The graph of $\phi_T(k,\mathbf{p}_\nu)$ for $\mathbf{p}_\perp=0$ is represented in Fig. 2 as a function of ν for two expansions, $m=1$ and $m=3$. In momentum space, the Bloch states are discontinuous functions of ν and their values are represented by thick bars in the figure. To provide a better description of the difference in the decay of $\phi^T(k,\mathbf{p}_\nu)$ for $m=1$ and $m=3$, the corresponding envelope functions have been added in as dashed lines. Figure 2 clearly shows that $\phi^T(k,\mathbf{p}_\nu)$ is of slower decay when m increases.

Our numerical experiments deal with the integral part of the method. This part is not only the most involved but also the first to be mastered before the iteration steps can be reasonably considered. The quantities obtained by algebraic methods[15,33] are thus ideal references to try to reproduce. Our goal in this testing part is twofold: (a) to provide *a posteriori* checks on the consistency of the formal expressions obtained in Sec. II, and (b) to learn on some of the problems occurring in the elaboration and practice of the procedure.

The conditions for these tests were the following. All

TABLE I. Numerical values of the parameters m, a_0, ζ, d_a, α_a, and β_a occurring in Eqs. (47) and (48); a_0 in Bohr units, $w_a=d_a(2\pi/\alpha_a)^{3/4}$, and $\beta_a=\pi^2(a_0^2\alpha_a)^{-1}$.

	For $m=1$, $a_0=1.915$,	$\zeta=1.156$	
$d_1=1.000\,00$,	$\alpha_1=0.362\,08$,	$w_1=8.502\,20$,	$\beta_1=7.432\,89$
	For $m=2$, $a_0=1.883$,	$\zeta=1.142$	
$d_1=0.430\,13$,	$\alpha_1=1.110\,91$,	$w_1=3.667\,55$,	$\beta_1=2.505\,65$;
$d_2=0.678\,91$,	$\alpha_2=0.197\,74$,	$w_2=13.383\,32$,	$\beta_2=14.076\,82$
	For $m=3$, $a_0=1.900$,	$\zeta=1.129$	
$d_1=0.154\,33$,	$\alpha_1=2.839\,47$,	$w_1=1.814\,29$,	$\beta_1=0.962\,84$;
$d_2=0.535\,33$,	$\alpha_2=0.517\,21$,	$w_2=6.507\,06$,	$\beta_2=5.285\,98$;
$d_3=0.444\,63$,	$\alpha_3=0.139\,98$,	$w_3=17.341\,45$,	$\beta_3=19.531\,09$

calculations were made with an inner region $d(0,p_{\text{in}})$ of radius $p_{\text{in}}=1$ a.u. and an outer region extending from p_{in} to p_{out} with $p_{\text{out}}=4$ a.u. The radii p_{in} and p_{out} have been chosen on the basis of the decay of $\phi^T(k,\mathbf{p})$ with $m=1$. The same algorithms were used in both the inner and the outer regions. Even though Fig. 2 points to the need for larger values of p_{in} and p_{out} in the case of $m=2$ and $m=3$, we have kept the same computational conditions for three cases, i.e., $m=1$, 2, and 3, in order to have a first idea of the sensitivity of the results with respect to these parameters. In the inner region, 31 p points and six abscissas for the θ variables have been used; in the outer region five p nodes were used, while the number of θ abscissas was the same as in the inner region. Finally, p_{in} was set equal to 7 and the number of k points in half the Brillouin zone was eight.

Equation (29) has been directly integrated as it reads. In the case of Eq. (43), pertaining to the total energy, a Gaussian function has been added and subtracted as indicated in Eq. (69) of Ref. 15, so as to improve upon the ill-conditioned numerical behavior of the integrand. The exponent B ($B=7.243$) of the function was the same for all three expansions, i.e., $m=1$, 2, and 3.

In the case of exchange a somewhat more involved treatment, which we outline hereafter, has been applied. The exchange contribution $X^T(k,\mathbf{p})$,

$$X_1^T(k,\mathbf{p})=X^T(k,\mathbf{p})=-(2\pi a_0)^{-1}\sum_{\mu}\int\frac{d\mathbf{q}_\perp}{q_\perp^2+(\mu+k'-k)^2}\int_{\mathrm{BZ}}dk'\,\theta(k')W(k',k,\mathbf{q}_{\mu+k'-k})\phi^T(k',\mathbf{p}-\mathbf{q}_{\mu+k'-k}),\quad(49)$$

is rewritten in a more compact form,

$$X^T(k,\mathbf{p})=\sum_{\mu}\int\frac{d\mathbf{q}_\perp}{q_\perp^2+(\mu+k'-k)^2}\times\int_{-1/4}^{1/4}dk'\,G(k',k,\mathbf{p},\mathbf{q}_{\mu+k'-k}),\quad(50)$$

where the limits of the k' integration are explicitly indicated and $G(k',k,\mathbf{p},\mathbf{q}_{\mu+k'-k})$ has been introduced to represent the numerator of Eq. (49),

$$G(k',k,\mathbf{p}-\mathbf{q}_{\mu+k'-k})=-(2\pi a_0)^{-1}W(k',k,\mathbf{q}_{\mu+k'-k})\times\phi^T(k',\mathbf{p}-\mathbf{q}_{\mu+k'-k}).\quad(51)$$

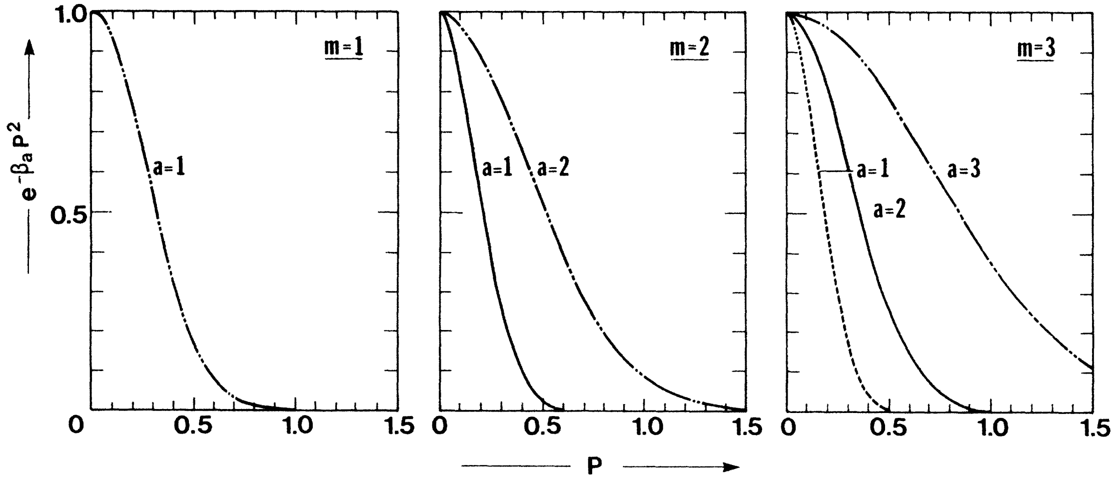

FIG. 1. Graphical representation of the various components, $\exp(-\beta_a p^2)$, entering Eq. (48) for the three expansions $m=1,2,3$. The values of the parameters are taken from Table I.

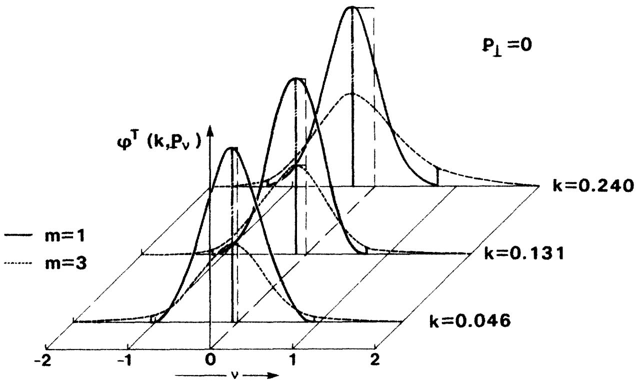

FIG. 2. Graph of the Bloch states as a function of v and k at $\mathbf{p}=0$. Gaussian expansions $m=1$ and 3 are represented. The selected values of k are 0.046, 0.131, and 0.240, and those for a_0 and β_a are taken from Table I. The scales are arbitrary.

Because $\theta(k')=2$ for $|k'|\leq\frac{1}{4}$, the singularities occur only for $\mu=0$ when $k'=k$. The terms for $\mu\neq0$ are directly integrated using the Gauss-Legendre quadrature. In the case $\mu=0$, the inner region of radius p_{in} is partitioned in a small circular region $d(0,\eta)$ of radius η and a ring (η,p_{in}). The integration in the ring is done using the Gauss-Legendre quadrature while an approximate analytical treatment is applied in $d(0,\eta)$.

The procedure amounts to choosing η small enough, $\eta\simeq0.04$, so that $G(k',k,\mathbf{p},\mathbf{q}_{\mu+k'-k})$ is nearly constant, with respect to $\mathbf{q}$, while the dependence in k' is approximated by a second-degree polynomial over subintervals of $[-\frac{1}{4},\frac{1}{4}]$,

$$G(k',k,\mathbf{p})\simeq a+bk'+c(k')^2, \tag{52}$$

in a given subinterval of $[-\frac{1}{4},\frac{1}{4}]$. The resulting expression is written as

$$X^T(k,\mathbf{p})=[X^T(k,\mathbf{p})]_\eta+[X^T(k,\mathbf{p})]_{\text{ring}}, \tag{53}$$

where, for a given subinterval S of the variable k' we have the following quantities to evaluate:

$$X_S^T(k,\mathbf{p})_\eta=\int_S dk'[a+bk'+c(k')^2]\int_0^\eta\frac{d\mathbf{q}_\perp}{\mathbf{q}_\perp^2+(k'-k)^2}\,. \tag{54}$$

The $\mathbf{q}_\perp$ integration can be made explicitly,[27]

$$X_S^T(k,\mathbf{p})_\eta=2\pi\int_S dk'[a+bk'+c(k')^2]\times[\ln|\eta^2+(k'-k)^2|-\ln|(k'-k)^2|\,], \tag{55}$$

and similarly the k' integrations in Eq. (55) have tabular entries[27] from which $X_S^T(k,\mathbf{p})_\eta$ can be given the following form:

$$\begin{aligned}X_S^T(k,\mathbf{p})_\eta=2\pi\Bigg\{&\ln(k^2+\eta^2)\left[[a+bk'+c(k')^2]k+\left[\frac{b+2ck'}{2}\right](k^2+\eta^2)+\frac{c}{3}k^3\right]\\&-2\ln|k|\left[[a+bk'+c(k')^2]k+\left[\frac{b+2ck'}{2}\right]k^2+\frac{c}{3}k^3\right]+2\eta^2k[a+bk+c(k')^2]\\&+2\eta\tan^{-1}\left[\frac{k}{\eta}\right][a+bk'+c(k')^2]+2\eta\tan^{-1}\left[\frac{k}{\eta}\right]\left[a+bk'+c(k')^2-\eta^2\frac{c}{3}\right]\Bigg\}_S\,.\end{aligned} \tag{56}$$

Computational checks have demonstrated the sensitivity of $[X^T(k,\mathbf{p})]_\eta$ with respect to the value of η which has to be small enough to make $G(k',k,\mathbf{p},\mathbf{q}_{\mu+k'-k})$ nearly constant in $d(0,\eta)$ but at the same time large enough to prevent dramatic losses of accuracy in the numerical evaluation of $[X^T(k,\mathbf{p})]_{\text{ring}}$.

Table II gives the results on the total energy and its Coulomb exchange and kinetic contributions obtained by the numerical procedures outlined above. The corresponding values by the algebraic approaches[15,33] are writ-

TABLE II. Ground-state RHF energies of $(\text{H})_x$ for different Gaussian expansions of the $1s$ hydrogenic function χ (data in atomic units). Corresponding values of algebraic approaches (Refs. 15 and 33) are given within parentheses.

m	Total Coulomb	Total exchange	Total kinetic	Total energy
1	−0.6488	−0.2919	0.4745	−0.4653
	(−0.6487)	(−0.2983)	(0.4745)	(−0.4726)
2	−0.7283	−0.2916	0.5149	−0.5050
	(−0.7307)	(−0.2983)	(0.5149)	(−0.5149)
3	−0.7445	−0.2900	0.5248	−0.5197
	(−0.7536)	(−0.2965)	(0.5248)	(−0.5253)

TABLE III. Selected values (in a.u.) of the energy band of $(\mathrm{H})_x$ for $m=3$. Corresponding values by algebraic approaches (Refs. 15 and 33) are given within parentheses.

	Coulombic energy	Exchange energy	Kinetic energy	Total energy
0.046	−0.4332	−0.6293	0.3570	−0.7056
	(−0.4289)	(−0.6365)	(0.3571)	(−0.7083)
0.131	−0.4731	−0.6009	0.4880	−0.5860
	(−0.4655)	(−0.6114)	(0.4871)	(−0.5926)
0.199	−0.5367	−0.5413	0.6939	−0.3841
	(−0.5318)	(−0.5531)	(0.6933)	(−0.3915)
0.240	−0.5907	−0.4643	0.8687	−0.1864
	(−0.5860)	(−0.4793)	(0.8684)	(−0.1856)

ten between parentheses. As expected the values obtained for $m=1$ are in closer agreement with the results provided by the algebraic approach than the other two ($m=2$ and $m=3$). The exchange contribution exhibits a noticeable departure which emphasizes the still insufficient treatment of the exchange singularity. The overall progressive degradation of the results when going from $m=1$ to $m=3$ is obvious and is due to the arbitrary small values chosen for p_{in} and p_{out}. Table III gives energies of the occupied band for $k=0.046$, 0.131, 0.199, and 0.240 in the case $m=3$. Corresponding values calculated with algebraic approach are given in parentheses.

Despite their preliminary nature, these data obtained by a straightforward numerical implementation of the equations of Sec. II compare consistently with the results of the algebraic approaches,[15,33] constitute a numerical verification of the expressions deduced in Sec. II, and provide useful indications as to where and what type of improvements are needed.

At this stage, absolute computing times are not representative of the future needs owing to the specific and straightforward code developed. However, it can already be appreciated as being a major advantage of the numerical approach that the computing resources were identical for the three cases ($m=1$, 2, and 3), contrary to what is noticed for the algebraic procedures. There the computing time increases significantly with the number of basis functions.

V. CONCLUDING REMARKS

General momentum-space RHF expressions for extended periodic model chains have been deduced and analyzed in this work. The separation of particle coordinates and the integral form of the final expressions obtained by transforming the direct-space RHF equations to momentum space are important properties to be used in the numerical determination of their solutions. Preliminary calculations on the $(\mathrm{H})_x$ model chain have been performed in order to test the consistency of the formalism and establish a first contact with the numerical problems raised by actual implementations of the project.

The mathematical characteristics of the momentum-space RHF equations are favorable for a direct numerical determination of their solutions and thereby go beyond the limitations to the accuracy obtainable in calculations relying on basis sets. The calculations reported on the integral part have given support to this assertion. However, several adjustments have to be made before considering the iteration steps and true numerical solutions can be claimed. During our attempts to reproduce the results obtained by algebraic approaches, the following points have been identified as requiring improvements.

(1) Generally, there is a need to use several concentric circular rings to perform more accurately and with greater versatility the integrations over the p and θ variables as well as to sample the one-electron states further away from the origin. Indeed, the Coulombic nature of the interactions in the potential terms induce singular points (cusps) in the direct-space graph of the one-electron states. A large part of the electronic energy is attached to these cusps and in momentum space this is carried over by the large p values.

(2) The computer time needed by a fully numerical approach aiming for high accuracy is expected to quickly become prohibitive. A procedure, where the classical algebraic methods (more effective in the description of the integrand tails in momentum space) and the numerical approach would be combined, seems appropriate to overcome these problems. It would also have the advantage of providing the explicit knowledge required to use analytical devices for summing the slowly convergent series.

(3) Exchange remains a problem; from our calculations it turns out that more flexibility has to be imparted in the approximation form of the integrand.

We are presently working on these points and hope to have soon a better control on the integration part to consider the iteration steps and ultimately be in a position to report on truly numerical HF solutions for quasi-1D model systems.

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