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A Combined Analytical and Numerical Strategy to Solve the Atomic Hartree–Fock Equations in Momentum Space

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The momentum representation offers new opportunities to obtain high quality approximate solutions to the Hartree–Fock equations. The self-consistent field method is applied here to the ground states of four- (Li^-, Be, and B^+) and ten- (F^-, Ne, and Na^+) electron atoms in momentum space. Analytical calculations using momentum space gaussian functions, together with Gauss quadrature and gaussian fit, are combined to compute the atomic Hartree–Fock orbitals.

I. INTRODUCTION

Since the beginning of the eighties, several authors have worked directly in momentum space to solve the Hartree–Fock (HF) equations for small atoms [1–8] and molecules [1, 2, 9–14]. The momentum space HF equations are derived by applying the Fourier transform to the usual position space expressions. This transformation being unitary, the representations of the HF equations in both spaces are equivalent and therefore contain the same information, but are expressed differently. Solving the momentum space HF equations also requires an iterative procedure, but the algorithms are different and offer specific advantages over the position space representation [1, 2, 9, 11]. This point will be stressed in the paper by describing an alternative strategy to avoid direct numerical calculations of the troublesome convolution products which are central to the momentum space HF equations.

The strategies previously developed have been either purely numerical or purely analytical. The numerical computations, using either FFT [1, 2] or quadratures [9–11, 14], have led to results very close to the HF limit. The drawbacks of these approaches are the need of large computer times and the difficulty to control the numerical accuracy. The approximate analytical solution to the HF equations obtained through a single iteration step, for atoms isoelectronic to He [3–5] and Be [6, 7] and for molecules such as H_2 [12] or HeH^+ [13] yields reasonably accurate results and is computationally fast. This direction is limited to a single iteration because the generation and calculation of expressions occurring in the next iterations become untractable. The purpose of this paper is to develop a mixed approach, numerical and analytical, to keep the convenience and the rapidity of the first iteration approach, as well as the possibility to carry out several iterations to converge towards the HF limit within a prescribed accuracy. The method is applied to the ground states of four- (Li^-, Be, and B^+) and ten- (F^-, Ne, and Na^+) electron atoms.

In Section II the momentum space closed-shell atomic HF equations and the principles of the momentum space variation-iteration method used to solve the HF equations are recalled. In Section III the analytical and numerical strategies are described in detail, and the results obtained for Li^-, Be, B^+, F^-, Ne, and Na^+ are discussed in

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Section IV. The paper ends with some considerations for future developments (Section V).

II. MOMENTUM SPACE CLOSED-SHELL ATOMIC HF EQUATIONS

The momentum space closed-shell atomic HF equations describing an atomic species of m electrons and of nuclear charge Z may be written as [9, 15]

$$\begin{aligned}\frac{p^2}{2}\phi_i(\mathbf{p})-\frac{Z}{2\pi^2}\int\frac{d\mathbf{q}}{q^2}\phi_i(\mathbf{p}-\mathbf{q})+2\sum_{j=1}^{m/2}\frac{1}{2\pi^2}\\ \times\int\frac{d\mathbf{q}}{q^2}W_{jj}^*(\mathbf{q})\,\phi_i(\mathbf{p}-\mathbf{q})-\sum_{j=1}^{m/2}\frac{1}{2\pi^2}\\ \times\int\frac{d\mathbf{q}}{q^2}W_{ij}^*(\mathbf{q})\,\phi_j(\mathbf{p}-\mathbf{q})\\ =\varepsilon_i\phi_i(\mathbf{p}),\qquad i=1,2,...,m/2,\end{aligned}\tag{1}$$

where $W_{ij}(\mathbf{q})$, the convolution product of $\phi_i(\mathbf{p})$ and $\phi_j(\mathbf{p})$, is defined as

$$W_{ij}(\mathbf{q})=\int d\mathbf{p}\,\phi_i^*(\mathbf{p})\,\phi_j(\mathbf{p}-\mathbf{q}).\tag{2}$$

The method to solve the HF equations in momentum space, Eq. (1), was first proposed by Navaza and Tsoucaris [9]; it is similar to a self-consistent field scheme and it basically includes four steps (a detailed account can also be found in Ref. [16]):

Step 1. Initialization of the procedure. A set of trial functions is chosen, and the corresponding orbital energies are calculated directly in momentum space,

$$\begin{aligned}\varepsilon_i=\int d\mathbf{p}\,\frac{p^2}{2}\phi_i^*(\mathbf{p})\,\phi_i(\mathbf{p})-\frac{Z}{2\pi^2}\int\frac{d\mathbf{q}}{q^2}W_{ii}(\mathbf{q})\\ +2\sum_{j=1}^{m/2}\frac{1}{2\pi^2}\int\frac{d\mathbf{q}}{q^2}W_{jj}^*(\mathbf{q})\,W_{ii}(\mathbf{q})\\ -\sum_{j=1}^{m/2}\frac{1}{2\pi^2}\int\frac{d\mathbf{q}}{q^2}W_{ij}^*(\mathbf{q})\,W_{ij}(\mathbf{q}),\\ i=1,2,...,m/2.\end{aligned}\tag{3}$$

Step 2. Iteration of the wavefunction. Knowing the functions $\phi_i^{(k)}(\mathbf{p})$ and energies $\varepsilon_i^{(k)}(\mathbf{p})$ at the kth iteration, the next iterates are derived according to the method originally proposed by Kellogg [17] and Svartholm [18], but modified in our case to deal with nonbound states as formulated in Eq. (4),

$$\begin{aligned}\phi_i^{(k+1)}(\mathbf{p})=\left[\frac{p^2}{2}-E_i^{(k)}\right]^{-1}\Bigg\{\frac{1}{2\pi^2}\Bigg(Z\int\frac{d\mathbf{q}}{q^2}\phi_i^{(k)}(\mathbf{p}-\mathbf{q})\\ -2\sum_{j=1}^{m/2}\int\frac{d\mathbf{q}}{q^2}W_{jj}^{*(k)}(\mathbf{q})\,\phi_i^{(k)}(\mathbf{p}-\mathbf{q})\\ +\sum_{j=1}^{m/2}\int\frac{d\mathbf{q}}{q^2}W_{ij}^{*(k)}(\mathbf{q})\,\phi_j^{(k)}(\mathbf{p}-\mathbf{q})\Bigg)\\ +C\phi_i^{(k)}(\mathbf{p})\Bigg\},\qquad i=1,2,...,m/2,\end{aligned}\tag{4}$$

where $E_i^{(k)}$ is related to the orbital energy $\varepsilon_i^{(k)}$ by the relation

$$E_i^{(k)}=\varepsilon_i^{(k)}-C,\qquad i=1,2,...,m/2.\tag{5}$$

Indeed, for bound states, the orbital energies, $\varepsilon_i^{(k)}$ ($E_i^{(k)}=\varepsilon_i^{(k)}$, $C=0$), have negative values and therefore $[p^2/2-E_i^{(k)}]$ is never equal to zero, so that Eq. (4) does not experience divergencies. For nonbound states ($\varepsilon_i\geqslant 0$) singularity arises and an energy shift C ($C>0$, $E_i^{(k)}<0$) is performed to avoid this singularity.

In a previous study [19] we have noted that, if the functions are directly used as received, the iterative scheme does not converge. Thus, at the end of each iteration step, the functions are systematically reorthonormalized with the Gram–Schmidt procedure that we have found to be best suited [6].

Step 3. Calculation of energies of the iterated functions. The orbital energies are calculated in momentum space using Eq. (3).

Step 4. End of iterations. Steps 2 and 3 are repeated until a given convergence threshold (energy, physical property, or mean-squared deviation between successive iterated functions) is reached.

III. ANALYTICAL AND NUMERICAL STRATEGIES

As first pointed out by Boys [20], the calculation of bielectronic integrals is greatly simplified with gaussian functions due to the property that the product of two gaussians yields another gaussian. Similarly, explicit calculations through first iteration, $k=1$ in Eq. (4), are not only possible with gaussians, but also relatively simple. This, in particular, allows us to use trial orbitals $\phi_i^{(0)}(\mathbf{p})$ coming from standard quantum chemistry packages and to introduce them directly in the iterative scheme. Over the last four years, we have accumulated results on atomic systems showing systematic and substantial qualitative and quantitative improvements already after one single iteration on their occupied atomic orbitals expressed as linear combinations of gaussian functions [3–7]. A few but equally encouraging results have recently been obtained on the H_2 [12] and HeH^+ [13] molecules with a similar type of treatment.

In addition to the possibility of an explicit mathematical treatment, the first iteration approach as described above has at least four additional advantages over a fully numerical approach: (i) the large saving in computation time due to the fact that the convolution products and other integrals occurring in Eqs. (3) and (4) can be evaluated explicitly, (ii) the orbitals after one iteration are expressed in terms of known transcendental functions and therefore can be evaluated for as many momentum values as desired, (iii) many properties can be evaluated numerically without difficulty, and (iv) the possibility to carry out an asymptotic analysis on the results to assess the improvements.

One of the drawbacks of the first iteration approach, however, is that computation of energy quantities, e.g., orbital and total energies, requires the evaluation of the integrals occurring in Eq. (4) on the basis of the $\phi_i^{(1)}(\mathbf{p})$. Unfortunately, the transcendental functions in terms of which the $\phi_i^{(1)}(\mathbf{p})$ are expressed at the end of the first iteration (especially the convolution product) do not lead to closed form expressions for these integrals and a numerical procedure is therefore needed. This constitutes a barrier to carrying out further iterations to improve the orbitals by approaching the HF limit.

In order to carry out further iterations, we propose a compromise between a fully numerical scheme and the simple first iteration approach. The scheme is based on the fact that at the end of each iteration the $\phi_i^{(k)}(\mathbf{p})$'s entail the main qualitative characteristics of the exact solution and most importantly the right asymptotic decay. The idea is thus to fit the iterated analytical functions $\phi_i^{(k)}(\mathbf{p})$ obtained at the kth step on a finite set of gaussian functions and then to use these fitted functions as a new set of trial functions $\phi_i^{g(k)}(\mathbf{p})$. The advantage is twofold. First, with exponents and linear coefficients that are specific for each orbital, the energies and functions are quickly improved. Second, the problematic convolution products and integrals are efficiently computed in terms of the gaussian functions that are obtained to represent the $\phi_i^{g(k)}(\mathbf{p})$'s.

At the end of the whole process, the properties which do not include convolution products in their expression (e.g., $\langle p^{-1}\rangle$, $\langle p\rangle$, $\langle p^2\rangle$, etc.) are obtained by direct numerical integration of the last iterated orbitals $\phi_i^{(k)}(\mathbf{p})$ to benefit from the functional characteristics imparted by the momentum space iteration.

The details of the steps involved in the scheme are given below and a corresponding flowchart is shown in Fig. 1.

Step 1. Initialization of the procedure. Trial functions $\phi_i^{g(0)}(\mathbf{p})$ come from the Fourier transforms of LCAO-GTO orbitals which are the SCF results of calculations performed with standard quantum chemistry packages (i.e., Gaussian90 [21]). Both position space and momentum space orbitals have the same orbital energies $\varepsilon_i^{(0)}$.

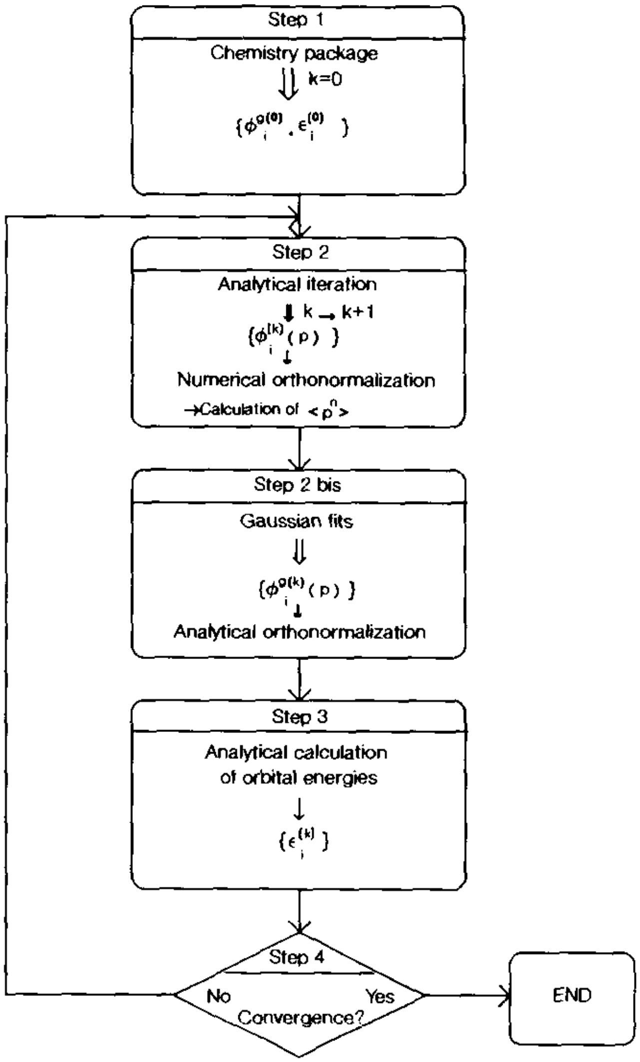

FIG. 1. Flowchart of the momentum space iterative scheme based on a gaussian fit.

Step 2. Iteration of the wavefunction. Using the Kellogg method [17], Eq. (4), the first iterated analytical functions $\phi_i^{(1)}(\mathbf{p})$ are calculated and orthonormalized numerically. The various quantities entering Eq. (4) are deduced when the trial orbitals $\phi_i^{(0)}(\mathbf{p})$ are expressed as linear combinations of Gaussian functions. As seen in the sequel, these quantities are expressible in terms of known transcendental functions. Two basic integrals, respectively denoted I_1 and I_2 have to be solved,

$$I_1(a, b, c, \alpha, \beta, \mathbf{q}) = \int d\mathbf{p}[ap_i p_j + bp_j + c]\, e^{-\alpha \mathbf{p}^2} e^{-\beta(\mathbf{q}-\mathbf{p})^2}, \qquad (6)$$

$$I_2(a, b, c, d, \alpha, \beta, \mathbf{q}) = \int \frac{d\mathbf{p}}{\mathbf{p}^2} \left[ap_i^2 p_j + bp_i p_j + cp_j + d\right] e^{-\alpha \mathbf{p}^2} e^{-\beta(\mathbf{p}-\mathbf{q})^2}, \quad (7)$$

where p_i and p_j stand for the cartesian components p_x, p_y, and p_z of the vector $\mathbf{p}$. The final expressions are given in the Appendix.

Step 2bis. Gaussian fit. The analytical functions $\phi_i^{(1)}(\mathbf{p})$ are represented as linear combinations of gaussian functions, $\phi_i^{g(1)}(\mathbf{p})$. This fit is carried out using a modified version of the Gausfit package [22] based on the work of Stewart [23] on gaussian fits of Slater functions. The resulting functions are analytically orthonormalized.

The radial part of $\phi_i^g(p)$ is expressed as a linear combination of spherical gaussians, which in the case of 1*s* and 2*s* orbitals may be written as

$$\phi_i^g(p) = \sum_{j=1}^{N} d_{ij} \exp(-\alpha_{ij} p^2), \quad (8)$$

and in the case of 2*p* orbitals as

$$\phi_i^g(p) = \sum_{j=1}^{N} d_{ij}\, p \exp(-\alpha_{ij} p^2). \quad (9)$$

Given a radial function $\phi(p)$ to fit, one minimizes the variance

$$\int_0^\infty dp\, p^2 \omega(p) [\phi_i(p) - \phi_i^g(p)]^2, \quad (10)$$

where $\omega(p)$ is a function which weights the contributions to the integral according to their expected importance. From several tests on Be and Ne we have found that the following weight functions are quite efficient:

$$\omega_{1s}(p) = 1 + p \quad (11)$$

and

$$\omega_{2s \text{ and } 2p}(p) = 1 + p^2. \quad (12)$$

Gaussian functions form a complete set, but they do not have the right asymptotic decay due to too low amplitudes in regions of large p values. Therefore representations in terms of gaussians are of much slower convergence than Slater functions. Since contributions from high momenta are essential to the energy, a second degree polynomial, Eq. (12), is used to introduce them in the valence orbitals.

A set of nine gaussians allows a satisfactory fit with low variance, Eq. (10), about 10^{-7} for the 1*s* and 2*p* orbitals and 10^{-6} for the 2*s* orbital. The valence orbitals with node(s) are slightly more difficult to fit. Under these conditions, the iterative scheme converges to results close to HF limit, but obviously it cannot approach it completely because the fit is based on a limited number of gaussian functions.

To prevent divergence and/or to speed up convergence at the $(k+1)$th iteration, it is suitable to build $\phi_i^{g(k)}(\mathbf{p})$ from a linear combination of the gaussian fit $\phi_i^{g(k-1)}(\mathbf{p})$ and the analytical iterated function $\phi_i^{(k)}(\mathbf{p})$ (see Fig. 1). This amounts to using a damping factor which is crucial when dealing with the valence orbitals of anions.

Step 3. Calculation of energies of the iterated functions. Orbital energies, Eq. (3), for the gaussian orbitals $\phi_i^{g(k)}(\mathbf{p})$ are calculated analytically in momentum space. Similarly to what has been done in Step 2, the analytical calculation of the energies, Eq. (3), requires the evaluation of an integral I_3:

$$I_3(a, b, c, d, \alpha) = \int \frac{d\mathbf{p}}{\mathbf{p}^2} \left[ap_i^2 p_j^2 + bp_i^2 + cp_j^2 + d\right] e^{-\alpha \mathbf{p}^2}, \quad (13)$$

where p_i and p_j stand for the cartesian components p_x, p_y, and p_z of the vector $\mathbf{p}$. The final expressions are given in the Appendix. As already explained, this leads to a very significant gain in computer time and does not require cumbersome checks on the numerical accuracy.

Step 4. End of iterations. The gaussian orbitals $\phi_i^{g(1)}(\mathbf{p})$ are used as trial functions, and Steps 2, 2bis, and 3 are repeated until a given convergence threshold (energy, physical property, or mean-squared deviation between successive iterated functions) is reached.

The whole process can be understood as a global improvement of the trial functions to obtain orbital shapes as close as possible to their HF limit. Properties other than energies are then computed directly with these final iterated functions by numerical integration, the numerical accuracy being then relatively easy to control. In the case of atoms isoelectronic to Be and Ne, the numerical calculations of $\langle p^n \rangle$ $(n = 1, 2)$ quantities and the orthonormalization factors (related to the overlap integrals), reduces to integrals depending on two variables θ and p in spherical coordinates:

$$I_{ii} = \int_0^\infty dp\, p^n \int_0^\pi d\theta \sin(\theta)\, \phi_i^*(p, \theta)\, \phi_i(p, \theta). \quad (14)$$

The evaluation of such integrals is carried out with the Gauss–Legendre quadrature method with a change of variable proposed by Ishikawa [8], whereas the angular part is calculated analytically.

TABLE I

Convergence towards HF Limits of the Atomic Orbital Properties (in a.u.) of Be Computed by the Momentum Space Method Using a "Nine-Gaussian" Fit

Be	STO-3G			STO-3G		
iteration	$\langle p^{-1}\rangle_{1s}$	$\langle p^{2}\rangle_{1s}$	ε_{1s}	$\langle p^{-1}\rangle_{2s}$	$\langle p^{2}\rangle_{2s}$	ε_{2s}
0	0.47680	13.195	−4.4840	2.1708	1.6489	−0.25404
1	0.47817	13.142	−4.7060	2.5557	1.1239	−0.30193
2	0.47602	13.376	−4.7296	2.6440	1.0258	−0.30746
3	0.47489	13.490	−4.7333	2.6721	1.0067	−0.30870
4	0.47441	13.537	−4.7337	2.6808	1.0015	−0.30911
5	0.47419	13.557	−4.7333	2.6836	1.0018	−0.30922
6	0.47412	13.564	−4.7332	2.6846	1.0018	−0.30922
7	0.47408	13.567	−4.7331	2.6843	1.0024	−0.30922
HF	0.47404	13.571	−4.7327	2.6851	1.0022	−0.30927

Be	4-31G			4-31G		
iteration	$\langle p^{-1}\rangle_{1s}$	$\langle p^{2}\rangle_{1s}$	ε_{1s}	$\langle p^{-1}\rangle_{2s}$	$\langle p^{2}\rangle_{2s}$	ε_{2s}
0	0.47430	13.540	−4.6749	2.3609	1.2475	−0.29200
1	0.47459	13.545	−4.7162	2.5712	1.0733	−0.30474
2	0.47428	13.558	−4.7276	2.6448	1.0249	−0.30777
3	0.47416	13.564	−4.7312	2.6710	1.0091	−0.30875
4	0.47411	13.566	−4.7329	2.6801	1.0042	−0.30907
5	0.47408	13.568	−4.7331	2.6814	1.0032	−0.30917
6	0.47406	13.569	−4.7331	2.6842	1.0030	−0.30920
7	—	—	—	—	—	—
HF	0.47404	13.571	−4.7327	2.6851	1.0022	−0.30927

Be	STO-3G		4-31G	
iteration	E_T	Vi	E_T	Vi
0	−14.352	−1.9668	−14.557	−1.9844
1	−14.563	−2.0209	−14.572	−1.9968
2	−14.572	−2.0118	−14.572	−1.9993
3	−14.572	−2.0053	−14.572	−1.9999
4	−14.572	−2.0024	−14.572	−2.0004
5	−14.572	−2.0010	−14.572	−2.0003
6	−14.572	−2.0005	−14.572	−2.0002
7	−14.572	−2.0003	—	—
HF	−14.573	−2.0000	−14.573	−2.0000

Note. The trial functions are expressed in the STO-3G and 4-31G basis sets.

IV. TESTS ON FOUR- AND TEN-ELECTRON ATOMS

In their ground states, the four-electron atoms Li^-, Be, and B^+ all correspond to the same electronic configuration $1s^2 2s^2$, and the ten-electron atoms F^-, Ne, and Na^+ to the electronic configuration $1s^2 2s^2 2p^6$. They are representative of the three electric states: cationic, neutral, and anionic. The electron charge distribution of cations B^+ and Na^+ is concentrated around the nucleus in position space, it corresponds to diffuse orbitals in momentum space. On the contrary, the electrons of the anions Li^- and F^- tend to occupy a larger portion of space around the nuclear center which corresponds to momentum space atomic orbitals with larger amplitudes near the origin. The neutral species Be and Ne obviously correspond to an intermediate behaviour.

In order to assess the quality of the atomic orbitals computed with the method just described over a large domain of momentum space, some physical properties of the orbitals $\phi_i^{(k)}(\mathbf{p})$ are computed at each iteration k. They are, total energy (E_T) and orbital energies ε_i ($i = 1s$, $2s$, or $2p$), Virial ratio (Vi), and the $\langle p^n\rangle_i$ ($n = -1, 2$ and $i = 1s$, $2s$, or $2p$) terms which probe preferentially the region of low momenta:

$$\langle p^n\rangle_i = \int d\mathbf{p}\, \phi_i^*(\mathbf{p})[p^n]\, \phi_i(\mathbf{p}). \tag{15}$$

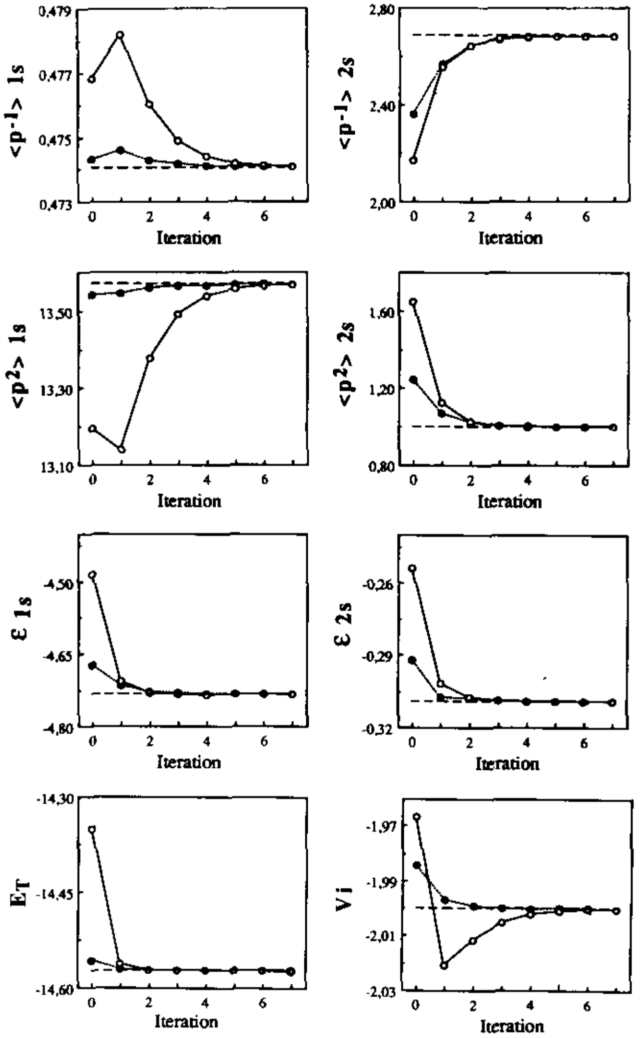

FIG. 2. Convergence towards HF limits (dotted lines) of the atomic orbital properties (in a.u.) of Be computed by the momentum space method using a "nine-gaussian" fit. The trial functions are expressed in the STO-3G (white discs) and 4-31G (black discs) basis sets.

TABLE II

Convergence towards HF Limits of the Atomic Orbital Properties (in a.u.) of Ne Computed by the Momentum Space Method Using a "Nine-Gaussian" Fit

Ne iteration	STO-3G			STO-3G		
	$\langle p^{-1}\rangle_{1s}$	$\langle p^2\rangle_{1s}$	ε_{1s}	$\langle p^{-1}\rangle_{2s}$	$\langle p^2\rangle_{2s}$	ε_{2s}
0	0.18027	90.937	−32.313	0.87082	9.7669	−1.7061
1	0.18095	90.359	−33.343	0.91135	9.9387	−2.0844
2	0.18029	91.566	−32.927	0.88996	10.517	−1.9569
3	0.18025	92.006	−32.846	0.89282	10.631	−1.9430
4	0.18025	92.165	−32.804	0.89568	10.609	−1.9361
5	0.18027	92.216	−32.788	0.89738	10.587	−1.9335
6	0.18030	92.230	−32.774	0.89942	10.534	−1.9295
7	0.18031	92.228	−32.771	0.89966	10.527	−1.9299
HF	0.17994	92.538	−32.773	0.90593	10.427	−1.9304

Ne iteration	4-31G			4-31G		
	$\langle p^{-1}\rangle_{1s}$	$\langle p^2\rangle_{1s}$	ε_{1s}	$\langle p^{-1}\rangle_{2s}$	$\langle p^2\rangle_{2s}$	ε_{2s}
0	0.17958	92.534	−32.696	0.90987	10.386	−1.9050
1	0.18035	92.035	−32.798	0.90202	10.470	−1.9339
2	0.18033	92.160	−32.776	0.89981	10.512	−1.9285
3	0.18031	92.201	−32.773	0.89978	10.536	−1.9294
4	0.18031	92.216	−32.772	0.89983	10.529	−1.9293
5	0.18031	92.230	−32.771	0.90013	10.524	−1.9295
6	—	—	—	—	—	—
7	—	—	—	—	—	—
HF	0.17994	92.538	−32.773	0.90593	10.427	−1.9304

Ne iteration	STO-3G			STO-3G	
	$\langle p^{-1}\rangle_{2p}$	$\langle p^2\rangle_{2p}$	ε_{2p}	E_T	Vi
0	0.47169	8.2861	−0.54306	−126.61	−2.0083
1	0.57258	7.2989	−0.96342	−128.32	−2.0498
2	0.54751	8.0545	−0.86172	−128.50	−2.0171
3	0.54814	8.2733	−0.85818	−128.53	−2.0075
4	0.54758	8.4004	−0.85366	−128.54	−2.0034
5	0.54737	8.4634	−0.85117	−128.54	−2.0017
6	0.54721	8.5105	−0.85085	−128.54	−2.0008
7	0.54711	8.5191	−0.85048	−128.54	−2.0007
HF	0.54733	8.5272	−0.85044	−128.55	−2.0000

Ne iteration	4-31G			4-31G	
	$\langle p^{-1}\rangle_{2p}$	$\langle p^2\rangle_{2p}$	ε_{2p}	E_T	Vi
0	0.52831	8.5386	−0.82761	−128.36	−2.0000
1	0.54442	8.4629	−0.85543	−128.53	−2.0039
2	0.54589	8.5069	−0.84994	−128.54	−2.0018
3	0.54686	8.5144	−0.85050	−128.54	−2.0010
4	0.54703	8.5202	−0.85054	−128.54	−2.0006
5	0.54706	8.5259	−0.85055	−128.54	−2.0006
6	—	—	—	—	—
7	—	—	—	—	—
HF	0.54733	8.5272	−0.85044	−128.55	−2.0000

Note. The trial functions are expressed in the STO-3G abd 4-31G basis sets.

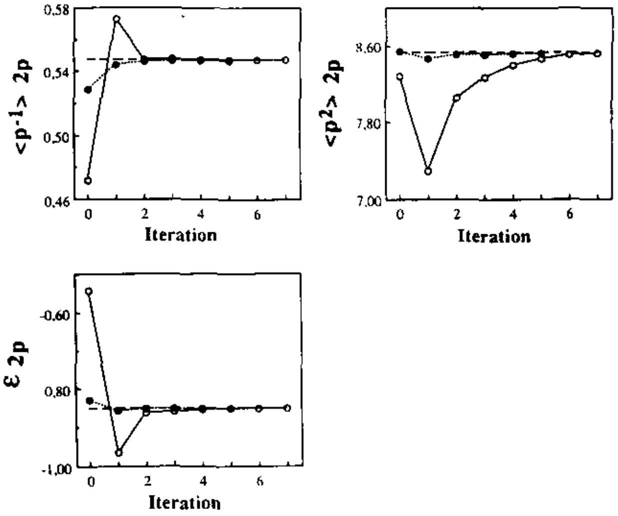

FIG. 3. Convergence towards HF limits (dotted lines) of the $2p$ atomic orbital properties (in a.u.) of Ne computed by the momentum space method using a "nine-gaussian" fit. The trial functions are expressed in the STO-3G (white discs) and 4-31G (black discs) basis sets.

The trial functions $\phi_i^{g(0)}(\mathbf{p})$ are obtained from the Gaussian90 program [21] using the standard STO-3G [24] and 4-31G bases [25] and they are used in the iterative scheme to generate new orbitals $\phi_i^{(k)}(\mathbf{p})$ obtained after k iterations. These two bases are considered in the comparison of the convergence of iterative cycles for trial functions of different qualities. In both cases, the number of the gaussian functions used in the fit is kept equal to nine. The properties are compared to the near HF limit values reported by Clementi and Roetti [26].

The evolution of the orbital properties through the iterations are presented in Table I and Fig. 2 for Be and in Table II and Fig. 3 for Ne (in Fig. 3 only the $2p$ orbital properties are plotted because the evolution of the $1s$ and $2s$ orbital properties of Be and Ne are *similar*). On the basis of these results, one notes that: (i) the convergence is monotonous, (ii) the method is stable in the sense that

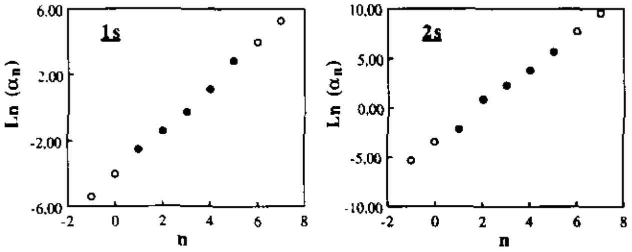

FIG. 4. Relation between the number (n) of gaussian functions and the logarithm of their exponents (α_n). The exponents of the functions obtained at the end of an iterative scheme for Be using a "five-gaussian" fit are denoted by black discs, whereas the extrapolated ones are denoted by white discs.

TABLE III

Convergence towards HF Limits of the Atomic Orbital Properties (in a.u.) of B^+ and Li^- Computed by the Momentum Space Method Using a "Nine-Gaussian" Fit

B^+ iteration	$\langle p^{-1}\rangle_{1s}$	$\langle p^2\rangle_{1s}$	ε_{1s}	$\langle p^{-1}\rangle_{2s}$	$\langle p^2\rangle_{2s}$	ε_{2s}	E_T	Vi
0	0.37284	21.376	−7.9863	1.6637	2.7999	−0.84925	−23.949	−1.9908
7	0.37091	21.903	−8.1856	1.7640	2.3282	−0.87373	−24.237	−2.0003
HF	0.37086	21.909	−8.1859	1.7662	2.3281	−0.87381	−24.238	−2.0000
Li^- iteration								
0	0.66059	7.0260	−1.9686	3.1212	0.80691	0.10225	−7.2133	−1.9209
7	0.65648	7.2248	−2.3222	6.3622	0.20219	−0.01463	−7.4280	−2.0002
HF	0.65644	7.2261	−2.3228	6.4347	0.20216	−0.01453	−7.4282	−2.0000

Note. The trial functions are expressed in the STO-3G basis set.

different starting functions ultimately lead to similar results, and (iii) results are very close to the HF limit, but not identical. This is due to the fact that, during the iterations, trial functions $\phi_i^{g(k)}(\mathbf{p})$ introduced in Eq. (4) are represented as finite linear combinations of gaussians. In Tables III and IV, respectively, for Li^- and B^+ and for F^- and Na^+, only the initial and the final results of the iterative procedure are reported. In these cases the trial gaussian functions $\phi_i^{g(0)}(\mathbf{p})$ are expressed in the standard STO-3G basis [24] only and a nine-gaussian fit is used. The trends obtained are very similar to those already observed for Be and Ne.

The good results obtained for the species, irrespective of their electric state (neutral, positive, or negative) allow us to conclude the generality of the method. Our recent results on negative atomic species [27], combined with the results obtained for diatomic molecules [12, 13], further support the hope that this momentum space approach is well suited to describe properly the electronic structures of molecular species, in general, and anions in particular.

From our results, a nine-gaussian fit has been found to be a good compromise between accuracy and computer time. In order to decrease the computer time, a smaller number of gaussians can be used for the fits. But this reduced number of gaussians yields a loss of accuracy, as it can be seen in the case of Be properties with a fit of five gaussians, $\phi_i(\mathbf{p})$-5G in Table V, where the iterative procedure starts with STO-3G orbitals. These results should be compared with the corresponding ones in Table I obtained with a nine-gaussian fit. In this case the computer time is five times longer than with five gaussians. However, a possible way out to improve the

TABLE IV

Convergence towards HF Limits of the Atomic Orbital Properties (in a.u.) of Na^+ and F^- Computed by the Momentum Space Method Using a "Nine-Gaussian" Fit

Na^+ iteration	$\langle p^{-1}\rangle_{1s}$	$\langle p^2\rangle_{1s}$	ε_{1s}	$\langle p^{-1}\rangle_{2s}$	$\langle p^2\rangle_{2s}$	ε_{2s}	$\langle p^{-1}\rangle_{2p}$	$\langle p^2\rangle_{2p}$	ε_{2p}	E_T	Vi
0	0.16407	109.93	−39.738	0.71645	15.172	−2.7473	0.39037	12.098	−1.3731	−159.43	−1.9878
9	0.16335	112.17	−40.757	0.77617	13.800	−3.0722	0.44732	11.814	−1.7972	−161.67	−2.0006
HF	0.16302	112.55	−40.760	0.77934	13.679	−3.0737	0.44741	11.816	−1.7972	−161.68	−2.0000
F^- iteration											
0	0.20136	73.174	−24.706	0.98375	7.6517	−0.59974	0.53273	6.4960	+0.37319	−97.613	−1.9731
6	0.20079	74.244	−25.828	1.0717	7.7058	−1.0721	0.72367	5.7316	−0.18039	−99.454	−2.0017
HF	0.20064	74.507	−25.830	1.0677	7.7689	−1.0744	0.72383	5.7277	−0.18085	−99.459	−2.0000

Note. The trial functions are expressed in the STO-3G basis set.

TABLE V

Comparison of the Quality of the Be Atom Properties

	$\phi_i^{(0)}(\mathbf{p})$	$\phi_i(\mathbf{p})$-5G	$\phi_i(\mathbf{p})$-9G	HF
$\langle p^2 \rangle_{1s}$	13.195	13.545	13.564	13.571
$\langle p^{-1} \rangle_{1s}$	0.47680	0.47417	0.47410	0.47404
ε_{1s}	−4.4840	−4.7253	−4.7342	−4.7327
$\langle p^2 \rangle_{2s}$	1.6489	1.0186	0.99790	1.0022
$\langle p^{-1} \rangle_{2s}$	2.1708	2.6766	2.6793	2.6851
ε_{2s}	−0.25404	−0.30736	−0.30922	−0.30927
E_T	−14.352	−14.560	−14.572	−14.573
Vi	−1.9668	−2.0010	−2.0008	−2.0000

Note. $\phi_i^{(0)}(\mathbf{p})$ (STO-3G orbitals), $\phi_i(\mathbf{p})$-5G (based on a fit of five gaussians, STO-3G orbitals as initial guess), and $\phi_i(\mathbf{p})$-9G (one-iteration based on a nine-gaussian fit of which exponents result from the even-tempered based extrapolation).

results obtained with a five-gaussian fit is to determine additional exponents using a linear relation, analogous to the one observed in the case of even-tempered basis set [28], between the logarithms of the gaussian exponents α_{ij}, Eq. (9), of the basis functions of the fits. Starting with the $\phi_i(\mathbf{p})$-5G of Table V, additional exponents (namely the four exponents at abscissas $\{-1, 0\}$ and $\{5, 6\}$ in Fig. 4) are obtained by an extrapolation of the linear relation between the logarithms of the five-gaussian exponents of the core (or the valence) orbitals. A new set of coefficients d_{ij}, Eq. (9), are then determined to compute the trial functions, $\phi_i^{(k)}(\mathbf{p})$-9G (Table V). In a straightforward program implementation, the overall computing time to reach a similar level of accuracy as that needed with nine gaussians directly from the beginning is approximately reduced by a factor of two.

V. FINAL REMARKS

The mixed analytical and numerical method, developed to solve the atomic HF equations in momentum space, tries to take best advantage (accuracy, convenience, and rapidity of evaluation) of the analytical natures of the trial and iterated functions. The numerical part is necessary to go beyond the first iteration in a manageable way in order to converge near the HF limits. The good quality of the results obtained in this way for neutral, cationic, or anionic species shows the generality of the method and is an incentive to extend it to treat polyatomic molecules.

APPENDIX A

In this appendix only the final expressions of integrals I_1, I_2, and I_3 are given. The principle of the deduction can be found in Refs. [3, 12], where all the details are given for the specific case of 1*s* orbitals.

$$I_1(a, b, c, \alpha, \beta, \mathbf{q}) = \int d\mathbf{p}[ap_i p_j + bp_j + c]\, e^{-\alpha \mathbf{p}^2} e^{-\beta(\mathbf{q}-\mathbf{p})^2}, \tag{16}$$

$$I_1(a, b, c, \alpha, \beta, \mathbf{q}) = \left(\frac{\pi}{\alpha+\beta}\right)^{3/2} \left[a\left(\frac{\beta}{\alpha+\beta}\right)^2 q_i q_j + b\left(\frac{\beta}{\alpha+\beta}\right) q_j + \frac{a}{2(\alpha+\beta)} + c \right] e^{-(\alpha\beta/(\alpha+\beta))\mathbf{q}^2}, \tag{17}$$

and

$$I_2(a, b, c, d, \alpha, \beta, \mathbf{q}) = \int \frac{d\mathbf{p}}{\mathbf{p}^2} [ap_i^2 p_j + bp_i p_j + cp_j + d]\, e^{-\alpha \mathbf{p}^2} e^{-\beta(\mathbf{p}-\mathbf{q})^2}. \tag{18}$$

$$\begin{aligned} I_2(a, b, c, d, \alpha, \beta, \mathbf{q}) &= 2\left(\frac{\pi^3}{\alpha+\beta}\right)^{1/2} \left[\frac{a\beta^3 q_i^2 q_j}{(\alpha+\beta)^3} \right. \\ &\quad \times \left(\frac{1}{2}\left(\frac{1}{t} - \frac{5}{2t^3} + \frac{15}{4t^5}\right) - \frac{15}{8t^6}\,\mathrm{Daw}(t) \right) \\ &\quad + \frac{((a/2)(2\delta_{ij}\beta q_i + \beta q_j) + b\beta^2 q_i q_j)}{(\alpha+\beta)^2} \\ &\quad \times \left(\frac{1}{2}\left(\frac{1}{t} - \frac{3}{2t^3}\right) - \frac{3}{4t^4}\,\mathrm{Daw}(t) \right) \\ &\quad \left. + \frac{((b/2)\,\delta_{ij} + c\beta q_j)}{(\alpha+\beta)} \left(\frac{1}{2t} - \frac{1}{2t^2}\,\mathrm{Daw}(t) \right) + d\,\mathrm{Daw}(t) \right] \\ &\quad \times e^{-(\alpha\beta/(\alpha+\beta))\mathbf{q}^2}/t. \end{aligned} \tag{19}$$

with

$$t^2 = \frac{\beta^2}{\alpha+\beta} \mathbf{q}^2 \tag{20}$$

and where δ_{ij} is the Kronecker delta, and $\mathrm{Daw}(t)$ denotes the so-called Dawson function [29]:

$$\mathrm{Daw}(t) = e^{-t^2} \int_0^t dx\, e^{x^2}. \tag{21}$$

And for I_3,

$$I_3(a, b, c, d, \alpha) = \int \frac{d\mathbf{p}}{\mathbf{p}^2} [ap_i^2 p_j^2 + bp_i^2 + cp_j^2 + d]\, e^{-\alpha \mathbf{p}^2}, \tag{22}$$

$$I_3(a, b, c, d, \alpha) = 2\left(\frac{\pi^3}{\alpha^5}\right)^{1/2} \left[d\alpha^2 + \frac{(b+c)\,\alpha}{6} + \frac{(1+2\delta_{ij})\,a}{20} \right]. \tag{23}$$

REFERENCES

1. S. A. Alexander and H. J. Monkhorst, *Int. J. Quantum Chem.* **32**, 361 (1987).
2. S. A. Alexander, R. L. Coldwell, and H. J. Monkhorst, *J. Comput. Phys.* **76**, 263 (1988).
3. J. Delhalle, J. G. Fripiat, and M. Defranceschi, *Ann. Soc. Sci. Bruxelles* **101**, 9 (1987).
4. J. Delhalle, J. G. Fripiat, and M. Defranceschi, *Bull. Soc. Chim. Belg.* **3**, 135 (1990).
5. M. Defranceschi and J. Delhalle, *European J. Phys.* **11**, 172 (1990).
6. L. De Windt, J. G. Fripiat, J. Delhalle, and M. Defranceschi, *Ann. Soc. Sci. Bruxelles* **105**, 89 (1991).
7. L. De Windt, J. G. Fripiat, J. Delhalle, and M. Defranceschi, *J. Mol. Struct.* (*Theochem.*) **254**, 145 (1992).
8. Y. Ishikawa, I. L. Aponte-Avellanet, and S. A. Alexander, *Int. J. Quantum Chem. Symp.* **23**, 209 (1989).
9. J. Navaza and G. Tsoucaris, *Phys. Rev. A* **24**, 683 (1981).
10. M. Defranceschi, M. Suard, and G. Berthier, *Int. J. Quantum Chem.* **25**, 863 (1984).
11. G. Berthier, M. Defranceschi, and J. Delhalle, in *Numerical Determination of the Electronic Structure of Atoms, Diatomic and Polyatomic Molecules*, edited by M. Defranceschi and J. Delhalle, NATO-ASI, Vol. C271 (Kluwer Academic, Dordrecht, 1989), p. 209.
12. P. Fischer, M. Defranceschi, and J. Delhalle, *Numer. Math.* **63**, 67 (1992).
13. P. Fischer, L. De Windt, M. Defranceschi, and J. Delhalle, Electronic structure of H_2 and HeH^+ computed directly in momentum space, *J. Chem. Phys.*, in press.
14. W. Rodriguez and Y. Ishikawa, *Chem. Phys. Lett.* **146**, 515 (1988).
15. W. H. Huo and E. N. Lassettre, *J. Chem. Phys.* **72**, 2374 (1980).
16. L. De Windt, J. Delhalle, and M. Defranceschi, *Int. J. Quantum Chem.* **45**, 609 (1993).
17. O. D. Kellogg, *Math. Ann.* **86**, 14 (1922).
18. (a) N. V. Svartholm, Ph.D. thesis, Lund, Stockholm, 1945; (b) N. V. Svartholm, *Ark. Mat. Astron. Fys. A* **35**, Nos. 7 & 8 (1947).
19. L. De Windt, Ph.D. thesis, Pierre et Marie Curie University, France, 1993.
20. S. F. Boys, *Proc. Roy. Soc. London Ser. A* **200**, 542 (1950).
21. M. J. Frisch, M. Head-Gordon, G. J. Trucks, J. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, D. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, *Gaussian90, Revision F*, Gaussian, Inc., Pittsburgh, PA, 1990.
22. M. Herman and R. E. Stanton, *Gausfit*, Quantum Chemistry Program Exchange, 11, 237 (1973).
23. R. F. Stewart, *J. Chem. Phys.* **50**, 2485 (1969).
24. W. F. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969).
25. W. F. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972).
26. E. Clementi and C. Roetti, *Atomic Data Nucl. Data Tables* **14**, 177 (1974).
27. L. De Windt, M. Defranceschi, and J. Delhalle, Electronic structure of Li^- and F^- calculated directly in momentum space, *Theor. Chim. Acta.*, in press.
28. M. W. Schmidt and K. Ruedenberg, *J. Chem. Phys.* **71**, 3951 (1979).
29. J. Spanier and K. B. Oldham, *An Atlas of Functions* (Hemisphere, Washington, DC, 1987), Chap. 42.