On the momentum-space approach to calculation of one-electron energy spectra and wave functions of atomic clusters

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Momentum-space approach to calculation of one-electron energies and wave functions proposed initially by Fock for a hydrogen atom and considered later by Shibuya, Wulfman, and Koga for diatomic molecules is applied to clusters composed of three and more atoms. The corresponding basis set in the coordinate space is of the Sturmian type since all the hydrogenlike orbitals in this set have a common exponent, i.e., correspond to the same energy (as opposed to one-electron atomic orbitals). By the examples of \( \text{He}_4^{+7} \) and \( \text{He}_6^{+11} \) cluster ions it is shown that increase in the number of orbitals in the set results in rapid convergence of eigenenergies and eigenfunctions of highly excited states. The momentum-space approach to the one-electron many-center problem may be used for various solid-state and quantum-chemical applications.

I. INTRODUCTION

In general, the one-electron many-center problem (i.e., the solution of the Schrödinger equation for an electron moving in the field of an arbitrary number of three-dimensional Coulomb centers) is known to have no exact analytical solutions. Making use of the variational approach does not allow for calculation of characteristics of excited states with controlled accuracy. Meanwhile, the knowledge of one-particle energy spectra and wave functions could facilitate the solution of numerous solid-state and quantum-chemical problems.

In the works \[1, 2, 3, 4\], the nonvariational approach based on the Fock representation \[5\] of the momentum-space Schrödinger equation has been proposed as an alternative to the usual position-space methods. However, in the papers \[1, 2, 3, 4\] the momentum-space approach has been applied to the diatomic molecules only (two-center problem).

The purpose of the present paper is to check the applicability of the momentum-space approach to the one-electron many-center problem, i.e., to calculation of one-electron energies and wave functions (including those for highly excited states) of systems composed of three or more Coulomb centers. Among other things this is important for calculations on atomic clusters. It is worthwhile to note that the many-center problem is basically different from the two-center one in that there appear three-center overlap integrals which are absent in diatomics, and it is not obvious in advance how the momentum-space approach will remain powerful in this case.

Below we present the results of calculations of the one-electron energy spectra and wave functions of \( \text{He}_4^{+7} \) and \( \text{He}_6^{+11} \) cluster ions within the momentum-space approach. The results obtained are verified by the direct numerical solution of the coordinate-space Schrödinger equation on a grid. We use atomic units \( e = m = \hbar = 1 \) throughout the paper.

II. MATHEMATICAL FRAMEWORK

In a momentum space, the Schrödinger equation \([-\Delta/2 - E + V(r)]\Psi(r) = 0\) for the energy \( E \) and the wave function \( \Psi(r) \) of an electron moving in an external potential \( V(r) \) is an integral equation for a Fourier transform \( \Psi(p) = (2\pi)^{-3/2} \int dr \Psi(r) \exp(-ipr) \) of \( \Psi(r) \) \[1, 2, 3, 4, 5\]:

\[
(|p|^2 + |p_0|^2)\Psi(p) = -2(2\pi)^{-3/2} \int dp' V(p - p')\Psi(p') ,
\]

where \(|p_0|^2 = 2|E|\) and \( V(p) = (2\pi)^{-3/2} \int dr V(r) \exp(-ipr) \). For a cluster composed of \( N_{\text{ion}} \) ions with charges \( Z_k \) and coordinates \( R_k \), where \( k = 1, ..., N_{\text{ion}} \) is the number of an ion in the cluster, one has \( V(r) = -\sum_k Z_k |r - R_k| \) so that \( V(p) = -4\pi(2\pi)^{-3/2}|p|^{-2} \sum_k Z_k \exp(-ipR_k) \), and hence Eq. \[1\] reads

\[
(|p|^2 + |p_0|^2)\Psi(p) = \pi^{-2} \sum_k Z_k \exp(-ipR_k) \int dp' |p - p'|^{-2} \exp(ip'R_k)\Psi(p') .
\]

The Fock transformation \[5\] projects the three-dimensional momentum space onto the four-dimensional sphere with a radius \(|p_0|\), where \(|p_0|\) is the energy-related momentum that enters Eqs. \[1\] and \[2\]. The function \( \Psi(p) \) is related
to its four-dimensional image $\Psi(\Omega)$ through

$$\Psi(p) = 4|p_0|^{5/2}(|p|^2 + |p_0|^2)^{-2}\Psi(\Omega) ,$$

where $\Omega$ stands for the set of three angles $(\alpha, \theta, \phi)$ resulting from the Fock transformation of a momentum vector $p = (|p|, \theta, \phi)$. Here the angles $\theta$ and $\phi$ have usual meaning and the angle $\alpha$ is related to $|p|$ through $\alpha = 2\arctan(|p|/|p_0|)$ so that $0 \leq \alpha < \pi$ for $0 \leq |p| < \infty$. The function $\Psi(\Omega)$ can be represented as

$$\Psi(\Omega) = \sum_{k,N} a_{kN} \exp(-ip R_k) Y_{N}(\Omega) ,$$

where $N = (n, l, m)$ stands for a set of three quantum numbers (principal $n = 1, 2, ..., $ orbital $l = 0, 1, ..., n - 1$, and azimuthal $m = -l, ..., l$) and $Y_{N}(\Omega)$ is a four-dimensional spherical harmonic defined as $Y_{N}(\Omega) = (-1)^l C_{nl}(\alpha) Y_{lm}(\theta, \phi)$. Here $C_{nl}$ are Gegenbauer polynomials and $Y_{lm}$ are usual three-dimensional spherical functions.

By the example of a diatomic molecule, it was shown in Ref. [3] that coefficients $a_{kN}$ in Eq. (4) satisfy the set of coupled homogeneous algebraic equations. Generalizing the consideration of Ref. [4] to the case of an arbitrary number $N_{ion}$ of ions in the cluster, we have

$$\sum_{j} H_{ij} a_j = 0 ,$$

where $i = (k, N)$, $j = (k', N')$,

$$H_{ij} = |p_0| S_{N'}^N (R_k - R_{k'}) - \sum_{k''} Z_{k''} \sum_{N''} \frac{1}{n''} S_{N''}^{N'} (R_k - R_{k''}) S_{N''}^{N'} (R_{k''} - R_{k'}) ,$$

$$S_{N'}^N (R_k - R_{k'}) = \int d\Omega Y_{N'}^N(\Omega) Y_{N'}(\Omega) \exp[ip (R_k - R_{k'})] .$$

The function $S_{N'}^N (R_k - R_{k'})$ can be expressed as<sup>1</sup> as an integral

$$S_{N'}^N (R_k - R_{k'}) = \frac{n}{|p_0|} \int dr \frac{\chi_N^* (r-R_k) \chi_{N'} (r-R_{k'})}{|r-R_k|}$$

over localized hydrogenlike orbitals

$$\chi_N (r) = (-1)^{n-l-1/2}|p_0|^{3/2}[(n-l-1)!/n(n+l)!]^{1/2}(2t)^l \exp(-t)L_{n-l-1}^{2l+1}(2t)Y_{lm}(\theta, \phi) ,$$

where $t = |p_0||r|$ and $L_{n-l}^{2l}$ are the associated Laguerre polynomials. Note that all orbitals $\chi_N (r)$ have a common exponent $|p_0|$, contrary to one-electron atomic wave functions. The functions $\chi_N (r)$ form the Sturmian basis set which, as noticed in Ref. [3], is a basis of a Sobolev space rather than a Hilbert space. All orbitals $\chi_N (r)$ correspond to the same energy, regardless of their quantum numbers.

Eq. (10) is the nonvariational equation. To find the expansion coefficients $a_{kN}$ and the energy parameter $|p_0|$, one should solve the nonlinear equation $\det(H_{ij}) = 0$ for $|p_0|$. Different solutions $|p_0|$ of this equation correspond to different eigenenergies $E_i$ and eigenfunctions $\Psi_i (r)$ of the one-electron Schrödinger equation in the coordinate space. Once the values of $|p_0|$ and $a_{kN}$ are obtained, the corresponding electron energy and wave function are, respectively, $E = -|p_0|^2/2$ and $\Psi_i (r)$.

$$\Psi(r) = \sum_{k,N} a_{kN} \chi_N (r-R_k) .$$

In general, there are four types of integrals over orbitals $\chi_N (r)$ in the matrix elements $H_{ij}$, see Eqs. (6) and (8). First is a one-center integral

$$\int dr \frac{\chi_N^* (r) \chi_{N'} (r)}{|r|} .$$

It appears if $k = k'$, see Eq. (8), and equals to $(|p_0|/n) \delta_{NN'}$, so that $S_{N'}^N (0) = \delta_{NN'}$. Second is a two-center integral

$$\int dr \frac{\chi_N^* (r) \chi_{N'} (r-R)}{|r|} .$$
that enters $S_N^{N'}(\mathbf{R}_k - \mathbf{R}_{k'})$ at $k \neq k'$. Next, it can be shown \footnote{2} that at $k = k' \neq k''$ the sum $\sum_{N''}$ in the second term of Eq. \footnote{3} equals to another two-center integral

$$\int dr \frac{\chi_N^*(r)\chi_{N'}(r)}{|r - \mathbf{R}|}$$

(13)

divided by $|p_0|$, where $\mathbf{R} = \mathbf{R}_{k''} - \mathbf{R}_k$. Finally, at $k \neq k', k \neq k''$, and $k' \neq k''$, the sum $\sum_{N''}$ in Eq. \footnote{4} is a three-center integral

$$\int dr \frac{\chi_N^*(r)\chi_{N'}(r - \mathbf{R}_1)}{|r - \mathbf{R}_2|}$$

(14)

divided by $|p_0|$, where $\mathbf{R}_1 = \mathbf{R}_{k''} - \mathbf{R}_k$ and $\mathbf{R}_2 = \mathbf{R}_{k'} - \mathbf{R}_k$.

In the case of a single ion ($N_{\text{ion}} = 1$) with a charge $Z$, there are only one-center integrals \footnote{11} in the matrix elements $H_{ij}$, and Eq. \footnote{5} allows for a simple analytical solution \footnote{3}. Since $H_{ij} = (|p_0| - Z/n)\delta_{N,N'}$ at $k = k'$, one has $|p_0| = Z/n$ and $E = -Z^2/2n^2$.

As one can see from Eqs. \footnote{6} and \footnote{3}, for a diatomic molecule ($N_{\text{ion}} = 2$), the matrix elements $H_{ij}$ include both one-center \footnote{11} and two-center \footnote{12}, \footnote{13} integrals. The analytical expressions for two-center integrals are rather complex. \footnote{4}. Hence, in order to solve Eq. \footnote{5} numerically, one should restrict himself to a finite number $M$ of orbitals $\chi_N(r)$ in the basis set. The authors of Ref. \footnote{2} applied the momentum-space approach to the molecular ion $\text{He}_4^+$. They calculated the energies of the ground $(1s\sigma_g)$ and one of the excited $(2p\sigma_u)$ states and showed that, as $M$ increases, both those energies decrease and converge to the corresponding `exact' values obtained by the analytical series solution in the coordinate space (see, e.g., Ref. \footnote{14}).

### III. RESULTS AND DISCUSSION

If the number of ions in the system is greater than two ($N_{\text{ion}} \geq 3$), there appear three-center integrals \footnote{14} in the matrix elements $H_{ij}$. In general, there are no exact analytical expressions for three-center integrals. However, because of the long-range nature of the Coulomb interaction, they are of the order of the corresponding two-center integrals. Hence, they can be neglected and have to be accounted for on an equal footing.

In order to check the applicability of the momentum-space approach to the one-electron problem in the case $N_{\text{ion}} \geq 3$, we have calculated the one-electron characteristics of several clusters with different ion charges and configurations. Below we present the results for chains composed of $N_{\text{ion}} = 4$ and 6 ions with charge $Z = 2$ each. From the one-electron viewpoint, these systems correspond to cluster ions $\text{He}_4^{1+}$ and $\text{He}_6^{1+}$ respectively. The linear form of the clusters was taken in order to facilitate the visualization of the wave functions in the coordinate space. We stress that our purpose was not to compute the energies and wave functions with an extremely high accuracy, as in Ref. \footnote{2} for a diatomic molecule, but just (i) to clarify the very possibility to apply the momentum-space approach to atomic clusters, i.e., to the one-electron many-center problem and (ii) to study the convergence rate at the initial stage of increase in the number $M$ of orbitals $\chi_N(r)$ in the basis set. So, we have restricted ourselves to $M = 5, 14,$ and 23. These values of $M$ correspond to account for all orbitals with $n \leq 2$; $n \leq 3$; and $n \leq 3, l \leq 3$ respectively. For each $M$, we have calculated the energies and the coordinate-space wave functions of $20 \div 30$ one-electron levels.

In Table I, we list the one-electron energies for the first 15 levels of the chain $\text{He}_4^{1+}$. One can see that the energy of each level decreases with $M$, this decrease being more pronounced for highly excited states. As one goes from $M = 5$ to $M = 14$, the energies of the lower four levels change by $(0.3 \div 0.5)\%$, while the energies of the higher levels change by $(9 \div 17)\%$. This is obviously due to larger weights of orbitals $\chi_N(r)$ with $n \geq 3$ in the wave functions of highly excited states. Note, however, that further increase in $M$ up to $M = 23$ results in an order of magnitude weaker change of the overall energy spectrum, less than by 0.015% for the lower four levels and by $(0.3 \div 2)\%$ for other levels. So, the convergence rate is very high, being comparable to that reported in Ref. \footnote{2} for $\text{H}_2^+$ molecule. Roughly speaking, an increase in the principal quantum number $n$ by one results in convergence of at least one more decimal digit, i.e., in at least one order of magnitude increase in the accuracy.

By the direct numerical solution of the coordinate-space Schrödinger equation on a grid, we have verified that all eigenenergies considered indeed converge to their ‘exact’ values. This is true for the eigenfunctions as well. Figure 1 shows the wave functions of the 5-th level calculated for different values of $M$. One can see that the wave functions for $M = 5$ and $M = 14$ differ considerably, while those for $M = 14$ and $M = 23$ are very close to each other. It is noteworthy that the wave function for $M = 23$ is visually indistinguishable from the ‘exact’ wave function obtained by the direct numerical integration of the Schrödinger equation. Note also that the small basis set ($M = 5$) is insufficient for even qualitative description of highly excited states. As one can see from Table I, in the case $M = 5$, the order
of levels in the energy spectrum appears to be broken starting with the 14-th level. The 14-th and 15-th levels are degenerate for \( M = 5 \), the corresponding wave functions being equal to zero at the line connecting the ions in the chain. Meanwhile, those levels are non-degenerate for both \( M = 14 \) and \( M = 23 \), in accordance with the 'exact' numerical solution. Figure 2 shows the wave functions of the 14-th level calculated for \( M = 14 \) and \( M = 23 \). They differ considerably, while the wave function for \( M = 23 \) practically coincides with the 'exact' wave function.

Figure 3 presents the one-electron energies of four lowest levels of the chain \( \text{He}^{+7}_4 \) as a function of the distance \( R_{23} \) between two inner ions, the values of \( R_{12} \) and \( R_{34} \) being fixed at \( R_{12} = R_{34} = 2.4 \). The first and the second cluster levels emerge from the first levels of the diatomic \( \text{He}^{+3}_2 \). As \( R_{23} \) decreases, the energy separation \( E_2 - E_1 \) increases due to stronger hybridization between molecular orbitals. The same is true for the splitting \( E_4 - E_3 \) between the fourth and the third cluster levels which both emerge from the second levels of the diatomic \( \text{He}^{+3}_2 \) as they approach each other. Note that \( E_2 - E_1 \) at a given \( R_{23} \) is much greater than \( E_4 - E_3 \). This is because of the different symmetry of the first and second diatomic orbitals (symmetrical and antisymmetrical, respectively). We have also solved the Schrödinger equation numerically at several values of \( R_{23} \), making use of the finite difference method on a fine grid, and verified the results obtained by the momentum-space approach.

Finally, we calculated the one-electron energies and wave functions for the first 29 levels of the chain \( \text{He}^{+11}_6 \). The results are similar to those presented above for the chain \( \text{He}^{+7}_4 \). Increase in \( M \) leads to the progressive decrease of all eigenenergies and their rapid convergence to the corresponding 'exact' values. Figure 4 shows the wave functions of the 10-th level computed for different values of \( M \). Again, as in the case of the chain \( \text{He}^{+7}_4 \), the wave functions for \( M = 5 \) and \( M = 14 \) differ considerably, while those for \( M = 14 \) and \( M = 23 \) are very close to each other, the wave function for \( M = 23 \) being almost identical with the 'exact' wave function. The eigenenergies are \( E_{10} = -2.414 \), \(-2.828 \), and \(-2.872 \) for \( M = 5 \), 14, and 23 respectively.

**IV. CONCLUSIONS**

In summary, we made use of the nonvariational momentum-space approach to calculate the one-electron energy spectra and wave functions of the ground and a large number of excited states of small atomic clusters. We have found that the one-electron characteristics converge rapidly with increase in the number of hydrogenlike orbitals in the basis set, each orbital having the same exponent, i.e., corresponding to the same energy. Our results show that the momentum-space approach to the one-electron many-center problem is rather powerful and may be considered as an interesting alternative to the position-space methods.

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[1] T. Shibuya and C.E. Wulfman, Proc. Roy. Soc. London A **286**, 376 (1965).
[2] T. Koga, J. Chem. Phys. **83**, 2328 (1985).
[3] T. Koga and T. Matsuhashi, J. Chem. Phys. **87**, 4696 (1987); **89**, 983 (1988).
[4] J. Avery and T. B. Hansen, Int. J. Quant. Chem. **60**, 201 (1996).
[5] V. Fock, Z. Phys. **98**, 145 (1935).
[6] The coefficients \( a_{MN} \) in the expansion of the wave function \( \Psi(\mathbf{r}) \) over the orbitals \( \chi_N(\mathbf{r}) \) should be scaled so that \( \Psi(\mathbf{r}) \) was normalized to unity.
[7] D. R. Bates, K. Ledsham, and A. L. Stewart, Philos. Trans. Roy. Soc. London A **246**, 215 (1954).
Table I. The one-electron energy spectra of the chain $\text{He}^{+7}_4$ calculated for different numbers $M$ of hydrogenlike orbitals $\chi_N(r)$ in the basis set. The value $M = 5, 14, \text{ and } 23$ corresponds to the basis set composed of $(1S,2S,2P)$, $(1S,2S,2P,3S,3P,3D)$, and $(1S,2S,2P,3S,3P,3D,4S,4P,4D)$ orbitals respectively. The distance between two inner ions is $R_{23} = 3$, the distance between each outer ion and its neighbour is $R_{12} = R_{34} = 2.4$. The energies and lengths are measured in atomic units.

| Level number | $M = 5$ | $M = 14$ | $M = 23$ |
|--------------|---------|---------|---------|
| 1            | -3.8961 | -3.9151 | -3.9157 |
| 2            | -3.8460 | -3.8584 | -3.8586 |
| 3            | -3.4430 | -3.4543 | -3.4543 |
| 4            | -3.4348 | -3.4433 | -3.4434 |
| 5            | -2.0881 | -2.3063 | -2.3149 |
| 6            | -1.9496 | -2.2043 | -2.2237 |
| 7            | -1.9496 | -2.2043 | -2.2237 |
| 8            | -1.8304 | -2.0570 | -2.0678 |
| 9            | -1.8304 | -2.0570 | -2.0678 |
| 10           | -1.7869 | -1.9504 | -1.9848 |
| 11           | -1.6536 | -1.9431 | -1.9532 |
| 12           | -1.4881 | -1.7440 | -1.7712 |
| 13           | -1.4881 | -1.7440 | -1.7712 |
| 14           | -1.4177 | -1.6308 | -1.6657 |
| 15           | -1.4177 | -1.5386 | -1.5621 |
Figure captions

Fig. 1. The wave functions $\Psi(x)$ of the 5-th one-electron level of the chain He$_4^{+7}$ calculated for different numbers $M$ of hydrogenlike orbitals $\chi_N(\mathbf{r})$ in the basis set, $M = 5$ (dashed line), $M = 14$ (dotted line), and $M = 23$ (solid line). The ion coordinates are (-3.9, 0, 0), (-1.5, 0, 0), (1.5, 0, 0), and (3.9, 0, 0) in atomic units. For $M = 23$, the wave function practically coincides with that obtained by the direct numerical integration of the coordinate-space Schrödinger equation.

Fig. 2. The same as in Fig.1, for the 14-th one-electron level of the chain He$_4^{+7}$. For $M = 5$, the wave function is zero at $y = 0$ and $z = 0$, see the text. For $M = 23$, the wave function practically coincides with that obtained by the direct numerical integration of the coordinate-space Schrödinger equation.

Fig. 3. The one-electron energies of the first four levels of the chain He$_4^{+7}$ versus the distance $R_{23}$ between two inner ions, the values of $R_{12}$ and $R_{34}$ being fixed at 2.4 each. Solid lines are the results of the momentum-space approach for $M = 23$ orbitals in the basis set. Circles are the numerical solutions of the Schrödinger equation on a grid.

Fig. 4. The wave functions $\Psi(x)$ of the 10-th one-electron level of the chain He$_6^{+11}$ calculated for different numbers $M$ of hydrogenlike orbitals $\chi_N(\mathbf{r})$ in the basis set, $M = 5$ (dashed line), $M = 14$ (dotted line), and $M = 23$ (solid line). The ion coordinates are (-6, 0, 0), (-4, 0, 0), (-1, 0, 0), (1, 0, 0), (4, 0, 0), and (6, 0, 0) in atomic units. For $M = 23$, the wave function practically coincides with that obtained by the direct numerical integration of the coordinate-space Schrödinger equation.
Figure 1
Figure 2
Figure 3
