

Linear method and basis set method for variational Monte Carlo ^4He ground state

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1 Introduction

The linear method is applied to optimize a variational wave function formed as a product of linear combinations of solutions of a two-body Schrodinger-like equation. Such a wave function results in convenient calculations for the derivatives of the wave function itself needed for the application of the linear method, and a easily scalable method on the number of variational parameters. The calculation is performed on the ground state of liquid ^4He .

2 Wave function

The system is described by the Hamiltonian:

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i<j} v(r_{ij}) \quad (1)$$

where $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ is the relative distance between particle i and j . The trial wave function, of the so called *basis set* method proposed by Vitiello & Schmidt [1], is written as a product of two-body terms

$$\psi_t(\{\mathbf{r}_i\}) = \prod_{i<j} f(r_{ij}) \quad (2)$$

where $f(r)$ is a linear combination of solutions of the two-body Schrodinger equation

$$-\frac{\hbar^2}{m} \nabla^2 f_n(r) + v(r) f_n(r) = \lambda f_n(r) \quad (3)$$

with $f(r) = \sum_n c_n f_n(r)$ and c_n as variational parameters.

By imposing the condition

$$f(r > L/2) = 1$$

where L is the side of the cubic box of particles, and the continuity of $f(r)$ at $L/2$, equation 3 become an eigenvalue equation, with f_n as the spherically symmetric eigenfunctions. Vanishing gradient and Laplacian of $f(r)$ at $r = L/2$ has also been imposed.

The solutions f_n can easily be found with the *Numerov's* shooting method [2], starting from $r = L/2$ and taking those eigenfunctions that goes to zero for $r \rightarrow 0$. The justification for such a variational ansatz is based on the fact that the potential $v(r)$ dominates at small pair separation and the relative interaction of two particle should be described by equation 3.

The potential used in the calculation is the simple Lennard-Jones of de Boer & Michels [3]: more complicated potential have been developed over the years for calculations of the ground state of liquid ^4He , resulting in slightly better results, but here the Lennard-Jones potential is used for his simplicity and to stress the importance of a better variational ansatz over a better potential. These results, then, can be compared with the ones from McMillan [4], where the Lennard-Jones potential has been used, combined with the very simple pair correlation factor

$$f(r) = e^{-\frac{1}{2}\left(\frac{b}{r}\right)^5} \quad (4)$$

with b as the only variational parameter. These results can also be compared with the results of Vitiello & Schmidt [5], where the basis set method has been used with a more modern potential.

3 Linear Method

A deeper overview of the linear method is presented in Motta *et al.* [6], which this work is heavily based on, with very handy calculations for local energy computed on derivatives of the wave function.

The basic idea of the linear method is to expand the wave function around the current parameter configuration \mathbf{p}_0 to the first order in the parameter variation:

$$|\psi(\mathbf{p})\rangle = |\psi_0\rangle + \sum_{j=1}^M \Delta p_j |\psi_j\rangle \quad (5)$$

where $|\psi_0\rangle \equiv |\psi(\mathbf{p}_0)\rangle$, Δp_j is the j component of the vector $\Delta \mathbf{p} \equiv \mathbf{p} - \mathbf{p}_0$, $|\psi_j\rangle = \left| \frac{\partial \psi}{\partial p_j}(\mathbf{p}_0) \right\rangle$ and M the number of parameters. Imposing some normalization constraint, in order to have orthogonality between $|\psi_0\rangle$ and $|\psi_j\rangle$, and minimizing the expectation value of the Hamiltonian with respect to the parameter variation, leads to a generalized eigenvalue equation of the form

$$H \begin{pmatrix} 1 \\ \Delta \mathbf{p} \end{pmatrix} = \varepsilon S \begin{pmatrix} 1 \\ \Delta \mathbf{p} \end{pmatrix} \quad (6)$$

where $H = H_{ij} = \frac{\langle \psi_i | H | \psi_j \rangle}{\langle \psi_0 | \psi_0 \rangle}$, $S = S_{ij} = \frac{\langle \psi_i | \psi_j \rangle}{\langle \psi_0 | \psi_0 \rangle}$ with $i, j = 1, \dots, M$, where now $|\psi_j\rangle$ are the re-normalized version of their previous definition. Solving equation 6 gives $M + 1$ eigenvalues and parameter variations eigenvectors, which can be easily rescaled to proper form $\begin{pmatrix} 1 \\ \Delta \mathbf{p} \end{pmatrix}$.

Such variations are stationary points of the energy expectation, and with $\varepsilon^{(i)}$ and $\Delta \mathbf{p}^{(i)}$ as the i th eigenvalue and eigenvectors of equation 6

$$\varepsilon(\mathbf{p}_0 + \Delta \mathbf{p}^{(i)}) = \varepsilon^{(i)} \quad (7)$$

where $\varepsilon(\mathbf{p}) = \frac{\langle \psi(\mathbf{p}) | H | \psi(\mathbf{p}) \rangle}{\langle \psi(\mathbf{p}) | \psi(\mathbf{p}) \rangle}$, which imply that the lowest eigenvalue corresponds to the minimum of the energy expectation.

All of this hints to solve equation 6, from a starting parameters configuration \mathbf{p}_0 , and recursively keep solving it with the new parameters configuration coming from the variations of the eigenvector corresponding to the lowest eigenvalue. Some precaution have to be taken in choosing the right eigenvector of variations, which is not always the lowest one. The calculations of the matrix elements H_{ij} have been performed via Monte Carlo integration. For more details on the microscopic estimators of the matrix elements check Motta *et al.* [6].

4 Results

The system under study is composed on $N = 125$ atoms of ^4He at the saturation density of 21.8 nm^{-3} . The number of the particle has been chosen so that the cutoff radius of the interaction, i.e. $L/2$, is large enough for the approximation $g(r > L/2) = 1$ to hold, where g is the radial distribution function. Setting the radial distribution function equal to 1 allows to count for the long range correction of the interactions between particle, left off by the introduction of the cutoff radius.

In order to compare the results with the one from Vitiello & Schmidt [5], the same number, 10, of spherically symmetric eigenfunctions f_n of equation 3 has been used, resulting in 10 parameters c_n . The solutions found are plotted in figure 4, enumerated from 1 to 10 starting from the one corresponding to the lowest eigenvalue.

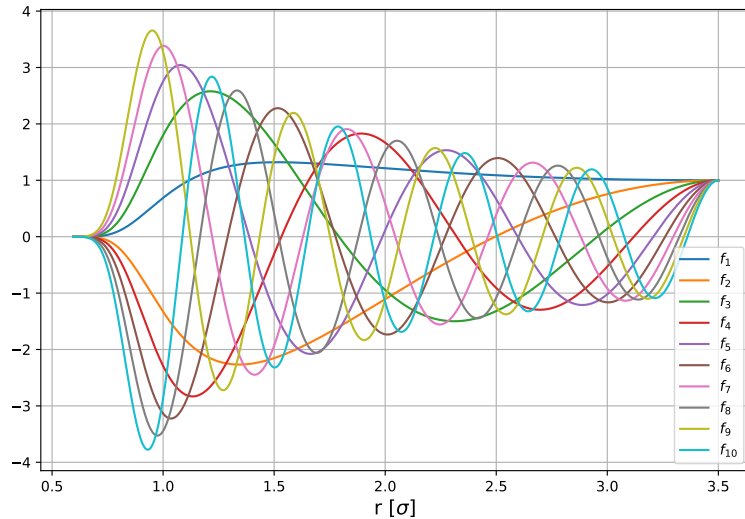


Figure 1: Spherically symmetric solutions of equation 3

As starting point for the iterative procedure the function $f = \sum_{i=1}^{10} c_n f_n$ has been fitted to the McMillan one of equation 4 with the energy minimizing value of $b = 1.18$ found in a previous work. The result for the first step integration, corresponding to the matrix element H_{00} , is $E_L = (-5.771 \pm 0.003) \text{ K/atom}$,

which is compatible with the result of McMillan and the previous work mentioned before. The results of the entire procedure are reported in figure 4, where the blue line represents the result of the local energy for the current parameter configuration, while the corresponding orange point represents the eigenvalue coming from the diagonalization of the Hamiltonian.

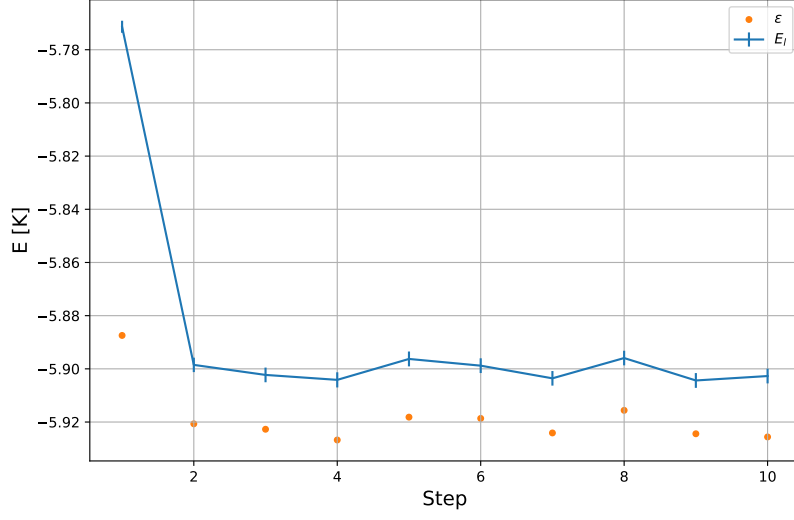


Figure 2: Linear method optimization

The iterative procedure converges basically after the first step, which is due to the fact that the starting point was already near the minimum, and it seems to retain a certain stability since all the results beyond the second step are compatible with each other in a 3σ interval.

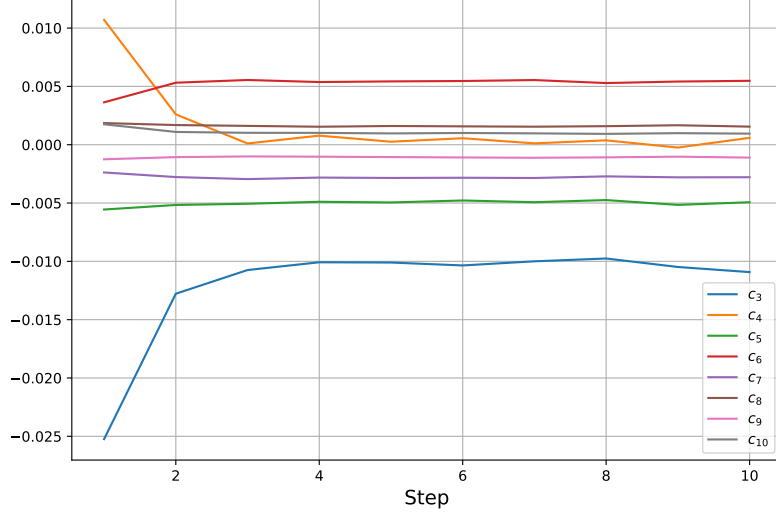


Figure 3: Flow of some of the variational parameters c_n over the iterative steps

The lowest value obtained is the one from third step and is equal to (-5.904 ± 0.003) K/atom, which is definitely worse than the value obtained by Vitiello & Schmidt [5] of (-6.17 ± 0.02) K/atom, obtained with the basis set method and a much more complicated and modern potential. However it is an improvement over the value of (-5.851 ± 0.007) K/atom, found in the same work by using the modern potential and the McMillan wave function of equation 4.

5 Conclusions

The combination of the basis set method and the linear method results in a powerful tool for variational calculations, since it provides a good variational ansatz for the wave function, while the linear method seems to be a very efficient algorithm to minimize the energy expectation with this kind of wave functions.

Few caveats have to be made. First of all the linear method in general does require more than one step to converge for non-linear wave functions and being based on the diagonalization of a matrix, the values of the matrix elements have to be very accurate for the algorithm to converge to the minimum, resulting in very computationally expensive Monte Carlo procedures: to obtain a smaller uncertainty more samples are needed and the computation of the Hamiltonian matrix element becomes computationally expensive.

Another problem of the linear method is the lack of an algorithmic way to choose the right eigenvectors coming from the Hamiltonian matrix diagonalization: in principal one should choose the one corresponding to the lowest eigenvalue, but sometimes that leads to large variations of $\Delta \mathbf{p}$, then the linear approximations of equation 1 doesn't hold anymore and the updated wave function bring worse results. In this work a few different criteria have been used to choose the right eigenvector, but none have made any kind of substantial dif-

ference. This is probably due to the fact that in this case the wave function is linear in its parameters. The safest choice would probably be to choose, between the eigenvectors with a lower energy than the local energy of the current step, the one with the lowest variance or the lowest absolute sum of the coordinates of the $\Delta\mathbf{p}$.

By far the biggest cause of error in the linear method is not taking enough Monte Carlo samples and having bad estimations for the matrix elements: the basis set method, in particular with its requirement of vanishing gradient at half of the size of the simulation cell, induces a very high correlation in the samples of the Markov chain sampler. As consequence a lot of samples, in the orders of millions, are required to obtain an accurate enough estimation of the matrix elements, increasing substantially the computational time. These problem could be mitigated by imposing a different boundary condition for the wave function.

The algorithm is also linearly scalable in the number of parameters, since adding parameters do not increase the computational cost of the sampling and scales linearly in the computation of the energy.

References

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