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F. Pederiva[1], M.H. Kalos[2], F. Reboredo[2], D. Bressanini[3], D.Guclu[4], L. Colletti[1], C.J. Umrigar[4]

[1]Dipartimento di Fisica, Università di Trento, Povo, Trento, Italy
[2]Lawrence Livermore National Laboratory, Livermore CA 94550
[3]Dipartimento di Scienze Chimiche e Ambientali, Università dell'Insubria, Como, Italy
[4]Cornell Theory Center, Cornell University, Ithaca NY 14853

We propose a new scheme for an approximate solution of the Schroedinger equation for a many-body interacting system, based on the use of pairs of walkers. Trial wavefunctions for these pairs are combinations of standard symmetric and antisymmetric wavefunctions. The method consists in applying a fixed-node restriction in the enlarged space, and computing the energy of the antisymmetric state from the knowledge of the exact ground state energy for the symmetric state. We made two conjectures: first, that this fixed-hypernode energy is an upper bound to the true fermion energy; second that this bound would necessarily be lower than the usual fixed-node energy using the same antisymmetric trial function. The first conjecture is true, and is proved in this paper. The second is not, and numerical and analytical counterexamples are given. The question of whether the fixed-hypernode energy can be better than the usual bound remains open.

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Introduction

Monte Carlo methods can be used to compute characteristics of many natural processes such as thermodynamic and transport properties of materials and, in particular, diffusion problems. This method is a fundamental tool for studying the many-body problem in quantum mechanics, in particular, the ground state energy of a many-body interacting system. The Schroedinger equation in real time is transformed into a diffusion equation in imaginary time, where the kinetic energy plays the role of a diffusion term and the potential is a source or sink of particles. Indeed, for positive imaginary times, the operator $\exp(-H\tau)$ acting on any state with no null projection c into the ground state $|g\rangle$ converges asymptotically to $c\exp(E_0\tau)\ |g\rangle$.[1] This provides a simple recipe to obtain the ground state energy of a many-body quantum system with a diffusion algorithm. However, there is an important limitation: since the ground state of a many-body system is a symmetric (bosonic) wavefunction, the evaluation of the energy of fermionic systems cannot be obtained only using this technique. Additional constraints must be added to force the wavefunctions to remain antisymmetric in the diffusion process[2]. In practice, the requirement of antisymmetry imposes boundary conditions upon the wavefunction. In this chapter we will describe a possible alternative to the standard fixed node approach based on the use of an extended space which is the product of the configuration space of the system under consideration by itself, in which a diffusion equation for pairs of points in the configuration space is implemented. Additional constraints are added in order to guarantee antisymmetry in the extended space. Such constraints in principle do not correspond to imposing a fixed-node constraint in the configuration space. In the next section we will review the fixed-node approximation. In the third section hypernodal functions in the product space will be introduced. The fourth section is devoted to the proof of upper bound properties for a restricted algorithm using hypernodal functions. The fifth section will present some results and some of the open questions related to this formalism.

Fixed node approximation

One of the earliest and still common approaches to impose antisymmetry is the so called fixed-node (FN) approximation[2]. In the standard FN-DMC, a trial wavefunction $\psi(\mathbf{r})$ is used to impose a fixed-node boundary condition (where $\mathbf{r}$ denotes the $3N$ coordinates of the electrons). The trial wavefunction must satisfy some conditions described below[3]. The walkers that generate the diffusion process are constrained to remain in a volume inside the nodes of $\psi(\mathbf{r})$. Thus,

the nodes act as a boundary having an infinite repulsive potential. Any point **r** inside a volume defined by the nodes, has images generated by symmetry operations on other volumes $S_n\mathbf{r}$ (where S_n are all possible permutations of electronic coordinates). Ideally the nodes of $\psi(\mathbf{r})$ must define volumes that expand the complete *3N* space Ω by applying all the symmetry operations of the group; that is, all the permutations of coordinates. This imposes some restrictions on the nature of the trial wavefunctions that can be used (i.e. for the ground state, they cannot have more nodes than required by symmetry.) Various techniques are used to contract these trial wavefunctions, typically including Slater determinants of appropriate basis functions and two-body correlations by way of Jastrow products. DMC in the fixed-node approximation yields the ground state wavefunction $\psi_{FN}(\mathbf{r})$ inside a volume defined by the nodes of $\psi(\mathbf{r})$ Since $\psi_{FN}(\mathbf{r})$ is obtained by projecting out the high-energy components of the original trial wavefunction compatible with its nodes, the corresponding expectation value of H must be less than or equal to that of the original trial wavefunction.

An antisymmetric wavefunction that expands the full volume Ω can be obtained from $\psi_{FN}(\mathbf{r})$ with the operation:

$$\psi^{*}_{FN}(S_n\mathbf{r}) = \sum_n \chi^{F}(S_n)\psi_{FN}(\mathbf{r}) . \qquad (1)$$

The function $\psi^{*}_{FN}(\mathbf{r})$ is, by construction, an antisymmetric wave function because $\chi^{F}(S_n)$ are the characters of the permutations operations in the antisymmetric representations of the symmetric group, *i.e.*, the $\chi^{F}(S_n)=1$ for even permutations and $\chi^{F}(S_n)=1$ for odd permutations. Therefore, the fixed-node approximation limits the search of the fermionic ground state to the subspace of linear combinations of antisymmetric wavefunctions that share the nodes of a trial wavefunction $\psi(\mathbf{r})$. Since the ground state of the true fermion problem $\psi_0(\mathbf{r})$ could have in principle different nodes than $\psi(\mathbf{r})$, we only obtain an upper bound of the fermionic ground state energy. The difference between this upper estimate and the true ground state energy is the *nodal error* of the fixed-node approximation.

Hypernodal functions

Various attempts have been explored to overcome the limitations imposed by the fixed-node approximation. Here we propose an algorithm which in principle should be able to go beyond the highly successful but nevertheless still limited fxed-node diffusion Monte Carlo.

We propose an alternative construction of the nodes in an expanded space that doubles the dimensions of the usual FN-DMC, and we impose fixed-node boundary conditions in this 6N-dimensional space. Instead of the usual fixed-node approximation we propose determining the nodes using functions of the form:

$$\begin{aligned}\psi^{b}_{HN}(R) &= \psi_A(\mathbf{r}_1)\psi_S(\mathbf{r}_2) + \psi_S(\mathbf{r}_1)\psi_A(\mathbf{r}_2) \\ \psi^{c}_{HN}(R) &= \psi_A(\mathbf{r}_1)\psi_S(\mathbf{r}_2) - \psi_S(\mathbf{r}_1)\psi_A(\mathbf{r}_2)\end{aligned} \tag{2}$$

where R=($\mathbf{r}_1$,$\mathbf{r}_2$), and the indexes 1 and 2 denote that the wavefunctions act on different subspaces with *3N* coordinates each. It is straightforward to see that, if ε_A and ε_S are the ground state energies of the fermionic and bosonic problem respectively, then

$$H\psi^{b,c}_{HN}(R) = (H_1 + H_2)\psi^{b,c}_{HN} = (\varepsilon_A + \varepsilon_S)\psi^{b,c}_{HN} \tag{3}$$

where H_1 and H_2 are identical except that H_1 acts on the set (1) of *3N* coordinates and H_2 on the set (2). It remains to be shown that the ground state solution within the nodes of functions of the form ψ^{b}_{HN} and ψ^{c}_{HN} have higher energy than $\varepsilon_A+\varepsilon_S$. That implies that the the energy of the lowest energy state of a domain inside the nodes of ψ^{b}_{HN} or ψ^{c}_{HN} is necessarily also the energy of a function with the structure of ψ^{b}_{HN} or ψ^{c}_{HN}.

A key step in the standard fixed-node approximation is the selection of an antisymmetric trial wavefunction, that is, an irreducible representation of dimension 1 of the group of all permutations of electronic coordinates[4]. The irreducible representations of dimension 1 are eigenvectors of every operator S_n with eigenvalues $\chi^{\nu}(S_n)$ denoted as characters. In general, for any *H*, if $\psi^{\nu}(\mathbf{r})$ belongs to an irreducible representation ν of *H* of dimension 1 of some group of symmetry operations S_n, the nodes of $\psi^{\nu}(\mathbf{r})$ transform as *H*. That is S_n *H*=*H* and if $\psi(\mathbf{r})$ =0, then

$$\psi(S_n\mathbf{r}) = \chi^{\nu}(S_n)\psi(\mathbf{r}) = 0 \tag{4}$$

for every S_n. The $\chi^{\nu}(S_n)$ are denoted as characters of the operator S_n on the representation ν. Thus all volumes enclosed by the nodes of an irreducible representation of dimension 1 $\psi^{\nu}(\mathbf{r})$ are equivalent by symmetry operations.

Accordingly, and provided that there are no additional accidental nodes, the full volume Ω can be expanded using Eq. (1). On the contrary, if $\psi(\mathbf{r})$ is a mixture of two or more representations i) the nodes and the volumes enclosed are no longer equivalent by symmetry, ii) there is no way to obtain by symmetry

operations the value of the ground state wavefunction outside a given volume; iii) since the volume are not equivalent, fixed nodes on different volumes give different energies.

In summary, in order to obtain an upper bound estimation of a ground state, it is key that the ground state belong to an irreducible representation of dimension 1 of the symmetry group of $H=H_1+H_2$. Using a trial wavefunction of the same irreducible representation will give an upper limit for the energy. Thus in order to prove the upper bound it is necessary and sufficient to demonstrate that functions of the form ψ^b_{HN} or ψ^c_{HN} are irreducible representations of dimension 1 of some symmetry group that expands the volume $\Omega\otimes\Omega$. Therefore, in the following section we will i) find the symmetry group ii) demonstrate that ψ^b_{HN} or ψ^c_{HN} are irreducible representations with dimension 1 of the a group and iii) extend the ground state fixed-hypernode wavefunction in all of the higher-dimensional space $\Omega\otimes\Omega$.

The extended Hamiltonian symmetries and some representations

In order to prove that ψ^b_{HN} and ψ^c_{HN} are irreducible representations of some group, we need to recall some properties of the symmetric group (the group of all possible permutations). Every permutation in the symmetric group commutes with the many-body Hamiltonian of identical particles. In quantum mechanics, irreducible representations are associated with quantum numbers or conserved quantities such as parity, angular momentum, etc. Good quantum numbers appear every time there is an operator that commutes with the Hamiltonian. There are two trivial 1-dimensional representations of the symmetric group. These representations are the identity (symmetric), with character 1 for every member of the group, and the antisymmetric representation, with character 1 for even and -1 for odd permutations. Depending on the order of the group (which is the number of permutations $N!$) there may be many other representations.
In the case of the antisymmetric wavefunctions the quantity conserved can be related to the operator

$$Q^F = \frac{1}{N!}\sum_n \chi^F(S_n)S_n \qquad (5)$$

that has eigenvalue 1 for every antisymmetric wavefunction and zero otherwise. It is possible to define analogously a bosonic operator Q^B which consists of the

sum of all permutations with eigenvalue 1. The operators Q^F and Q^B can be rewritten as:

$$\begin{aligned} Q^F &= [1 - S_{ij}][\Sigma E] = [\Sigma E][1 - S_{ij}] \\ Q^B &= [1 + S_{ij}][\Sigma E] = [\Sigma E][1 + S_{ij}], \end{aligned} \tag{6}$$

where S_{ij} is any single pair exchange and [ΣE] the sum over all even permutations.

Suppose that $S_{ij}(1)$ is any permutation of two coordinates i,j on the space (1) and $S_{lm}(2)$is another permutation acting on space (2). Since these two operators commute, the character table of the group generated by the product can be factored out as a product of the character tables of the subgroups. Moreover, the irreducible representations of the product group are products of the irreducible representations of the factors. Thus, since we know two irreducible representations of the symmetric group we can trivially guess four irreducible representations of the product group. They are given by:

$$\begin{aligned} &\psi^a_{HN}(R) = \psi_S(\mathbf{r}_1)\psi_S(\mathbf{r}_2) \\ &\frac{\psi^b_{HN}(R) + \psi^c_{HN}(R)}{2} = \psi_S(\mathbf{r}_1)\psi_A(\mathbf{r}_2) \\ &\frac{\psi^b_{HN}(R) - \psi^c_{HN}(R)}{2} = \psi_A(\mathbf{r}_1)\psi_S(\mathbf{r}_2) \\ &\psi^d_{HN}(R) = \psi_A(\mathbf{r}_1)\psi_A(\mathbf{r}_2) \end{aligned} \tag{7}$$

There is a symmetry operation of the Hamiltonian that we have not considered so far: the exchange of all coordinates in the subsets (1) and (2) denoted by the operator P. Applying P to the irreducible representations of the product of permutations in Eq. (7) one immediately finds that P mixes the second and third representation of the subgroup of all permutations in Eq.(7). Therefore, functions of the form ψ^b_{HN} and ψ^c_{HN} generate an irreducible representation of dimension 2 of the group all symmetry operations of H, and it is possible to define the operator T,

$$T(b,c) = \; Q^F(1)\, Q^B(2) \; + \; Q^B(1)\, Q^F(2) \tag{8}$$

which is the associated projector into that subspace [see Eq.(6)]. This case is analogous to the group of continuous rotations in spherical symmetry. The representations have dimensions larger than one for angular momentum $l > 0$.

Because ψ^{b}_{HN} and ψ^{c}_{HN} belong to the same representation they give rise to degenerate states. Eigenfunctions within a representation with dimension larger than 1 can be classified according to a symmetry operation in the group. The exchange operator P can be used to assign an additional quantum number to them with eigenvectors of the form ψ^{b}_{HN} and ψ^{c}_{HN}. The associated projectors are:

$$\begin{aligned} T(b) &= \frac{(E+P)}{2} T(b,c) \\ T(c) &= \frac{(E-P)}{2} T(b,c) \end{aligned} \tag{9}$$

Physically, one can also remove these degeneracies by breaking the symmetries of the Hamiltonian. We will follow this path to find a group that has ψ^{b}_{HN} and ψ^{c}_{HN} as distinct irreducible representations. For that we consider only the permutations that commute with P, that is, only permutations of the form $S_n(1).S_n(2)$.

The group of all $S_n(1).S_n(2)$ is an isomorphism of the symmetric group of the S_n acting in a single space. Thus they have the same character tables. Multiplying every $S_n(1).S_n(2)$ by E or P defines a larger group of order $2N!$. Taking advantage of the knowledge of two irreducible representations of the symmetric group one can generate the projectors of four representations of the product group. Since, as in the previous case the projectors are the product of the subgroups projectors:

$$\begin{aligned} T(a) &= (P+E)Q(+) \\ T(b) &= (P+E)Q(-) \\ T(c) &= (P-E)Q(-) \\ T(d) &= (P-E)Q(+) \end{aligned} \tag{10}$$

with

$$\begin{aligned} Q(1,2)(\pm) &= \sum_{n} \chi^{B,F}(S_n) S_n(1).S_n(2) = \\ &= [1 \pm S_{ij}(1) S_{ij}(2)][\Sigma E(1).\Sigma E(2)]/N! \\ &= [\Sigma E(1).\Sigma E(2)][1 \pm S_{ij}(1) S_{ij}(2)]/N! \end{aligned} \tag{11}$$

where $S_{ij}(\sigma)$ is any single pair permutation acting on the set of coordinates σ, $[\Sigma E(1).E(2)]$ is the sum over all the products of even permutations, and $N!$ is the total number of permutations. By construction $Q(\pm)$ are projectors on the symmetric and the antisymmetric representation of the group generated by $S_n(1).S_n(2)$. Since the even permutations are a subgroup of the symmetric group one has that $[\Sigma E(1).E(2)][\Sigma E(1).E(2)]=[\Sigma E(1).E(2)]\ N!/2$ and one can therefore show that $Q(1,2)\ Q(1,2) = Q(1,2)$.

It is easy to see that

$$\begin{aligned} T(b,E)\psi^{b}_{HN} &= \psi^{b}_{HN} \\ T(b,E)\psi^{c}_{HN} &= 0 \\ T(c,E)\psi^{c}_{HN} &= \psi^{c}_{HN} \\ T(c,E)\psi^{b}_{HN} &= 0 \end{aligned} \tag{12}$$

Also any symmetry operation outside this reduced group such as $S_n(1).S_m(2) = S_n(1).S_n(2).S_n(2).S_m(2) = S_n(1).S_n(2).S_k(2)$ may be applied to ψ^{b}_{HN}:

$$\begin{aligned} S_n(1).S_n(2).S_k(2)\psi^{b}_{HN} &= \psi^{b}_{HN} && S_n, S_k \text{ even} \\ S_n(1).S_n(2).S_k(2)\psi^{b}_{HN} &= -\psi^{b}_{HN} && S_n \text{ odd}, S_k \text{ even} \\ S_n(1).S_n(2).S_k(2)\psi^{b}_{HN} &= \psi^{c}_{HN} && S_n \text{ even}, S_k \text{ odd} \\ S_n(1).S_n(2).S_k(2)\psi^{b}_{HN} &= -\psi^{c}_{HN} && S_n, S_k \text{ odd} \end{aligned} \tag{13}$$

Similar rules are found for ψ^{c}_{HN}. Therefore, only if $S_k(2)$ is odd are the representations ψ^{b}_{HN} and ψ^{c}_{HN} mixed. In other words, we only need to remove the symmetries $S_n(1).S_n(2).S_k(2)$ when $S_k(2)$ is odd to split ψ^{b}_{HN} and ψ^{c}_{HN}. Since we know that ψ^{b}_{HN} is an eigenvector of all $S_n(1).S_n(2).S_k(2)$, and of P for $S_k(2)$ even, and that the eigenvalues are the same for different even $S_k(2)$, we can write the associated projector that includes these symmetries as

$$\frac{1}{2N!}\sum_{S_k \text{ even}} T(b/c,E)S_k(2) = T(b/c)\frac{1}{2N!}[\Sigma E(2)] \tag{14}$$

With a little work it can be shown now that the projectors $T(b)$ and $T(c)$ defined in Eq. (9) and (14) are indeed identical. Therefore, $T(b)$ and $T(c)$ project into a representation of dimension 1 of a group, namely the one formed by all P

and all $S_n(1).S_n(2).S_k(2)$ with $S_k(2)$ even. Thus ψ^b_{HN} and ψ^c_{HN} are irreducible representations of dimension 1 of a subgroup of symmetries of H and the volume enclosed by their nodes can be extended to the complete space by application of the operations of the subgroup. That is what we wanted to prove. In other words, just as the permutations are enough to construct an antisymmetric function over the full space, so, in our larger space, the permutations plus interchange of the two sets of coordinates serves the same purpose.

Results

The fixed-hypernode algorithm is a straightforward extension of the standard fixed-node procedure. Instead of working with a single walker, we use pairs of walkers, each one defined in the subspaces 1 and 2 respectively. Each walker is drifted/diffused according to the usual prescription using as importance function either ψ^b_{HN} or ψ^c_{HN}. Moves are rejected whenever the importance function changes sign, and the energy is projected out of the importance function. The outcome is an upper bound for the sum of the energies of the symmetric and antisymmetric ground states. Additionally, one needs to compute the energy of the symmetric state by means of standard Diffusion Monte Carlo. The difference between this quantity and the FHN eigenvalue will give an upper bound for the ground state of the fermionic state.

The important issue is to assess the quality of this upper bound with respect to the standard FN value. In fact, it can be easily seen that walkers subject to the FHN constraint are not in principle constrained within a nodal pocket in the configuration space, and more space can be explored.

However, this fact in itself is not enough to guarantee that the FHN upper bound is better (or worse) than the FN one

Numerical experiments were performed on two different systems. The first was a N=6 electrons quantum dot, defined by the Hamiltonian[5]

$$H = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m_e m^*}\nabla^2 + \frac{1}{2}m_e m^* \omega^2 r_i^2 \right) + \frac{e^2}{\varepsilon}\sum_{i<j}\frac{1}{|r_i - r_j|} \qquad (15)$$

where m^* =0.067 and ε=12.4 are the effective mass and effective dielectric constant which approximate electrons in GaAs, and ω=3.32meV is the confinement constant of the dot. For this system the FN energy in effective atomic units (effective Hartrees) is 7.6001(1). The FHN eigenvalue is 14.752(5), and the energy for the equivalent symmetric system is 7.1086(1), giving as an estimate for the antisymmetric ground state 7.643(3), which is higher than the fixed node estimate.

More tests of this procedure have been performed on the Be atom, using different importance functions with different degrees of optimization[6]. The results are summarized in Table I. The wavefunctions labelled as A, B and C in the table are obtained using in the construction of the hypernodal function, antisymmetric functions which are respectively a one-determinant trial wavefunction with incorrect cusp and non-optimized parameters (A), a one-determinant wavefunction with correct cusp and optimized parameters (B), and a four-determinant wavefunction with correct cusp and optimized parameters (C).

Table I. Fixed-hypernode results for the Be atom

Wavefunction	*DMC*	*VMC*
Boson	-19.26439(1)	-19.27439(1)
A FN	-14.6578(3)	-14.615(2)
A FHN	-33.9323(3)	-33.890(2)
A FHN-Boson	-14.6579(3)	-14.616(2)
B FN	-14.6571(3)	-14.6400(2)
B FHN	-33.9313(3)	-33.9144(2)
B FHN-Boson	-14.6570(3)	-14.6401(4)
C FN	-14.66721(1)	-14.6665(4)
C FHN	-33.94512(20	-33.94158(2)
C FHN-Boson	-14.66719(3)	-14.6665(2)
Exact[7]	-14.66736	

As it can be seen from the table, the results are in contrast with the conjecture that the FHN upper bound is lower than the standard FN one. In particular, it can be noticed that the FHN estimates for the Fermion eigenvalue (i) do strongly depend on the choice of the *antisymmetric function* used to build the hypernodal function and (ii) are essentially the same as the FN estimates for that particular antisymmetric function. This result would suggest that although the nodal properties of the hypernodal functions are not directly related to the

nodes of the antisymmetric function used, some of this information is passed into the doubled space. This point is not completely clarified at present.

It is however possible to show that in general using a good antisymmetric trial function for building an hypernodal function does not lead in principle to better eigenvalues. In fact, let us assume that we know an approximate antisymmetric trial whose nodes are *exact*. For instance, let us consider the problem of a particle in a two dimensional square box of side 1, seeking an estimate of the eigenvalue for the first spatial antisymmetric solution. Let φ_S be an approximation of $\cos(\pi x/2)$. We can build four approximations of the exact degenerate antisymmetric eigenstates, each one with an *exact node*:

$$\begin{aligned}
\psi_1 &= \varphi_S(x)\sin(\pi y) \\
\psi_2 &= \varphi_S(y)\sin(\pi x) \\
\psi_3 &= \varphi_S(y)\sin(\pi x) - \varphi_S(x)\sin(\pi y) \\
\psi_4 &= \varphi_S(y)\sin(\pi x) + \varphi_S(x)\sin(\pi y)
\end{aligned} \tag{16}$$

Obviously, if we used FN-DMC for computing the expectation value of the Hamiltonian using any of these function, we would obtain the exact eigenvalue. On the other hand, if we build an hypernodal function starting from a symmetric function $\Psi_S = \varphi_S(x)\,\varphi_S(y)$:

$$\Psi_{HN} = \Psi_S(x_1, y_1)\Psi_3(x_2, y_2) - \Psi_S(x_2, y_2)\Psi_3(x_1, y_1) \tag{17}$$

it is easy to see that the hypernodes are given from the following expression:

$$\frac{\sin(\pi y_1)}{\varphi_S(y_1)} - \frac{\sin(\pi x_1)}{\varphi_S(x_1)} - \frac{\sin(\pi y_2)}{\varphi_S(y_2)} + \frac{\sin(\pi x_2)}{\varphi_S(x_2)} = 0 \tag{18}$$

which in general has hypernodes which (i) depend on the choice of φ_S and (ii) *do not coincide with the exact hypernode*. Therefore, the estimate of the energy for the antisymmetric state will be *worse* than the corresponding fixed-node estimate. So, in general, it is possible to build hypernodal function with a wrong hypernodal surface starting from functions with the correct nodal surface.

However, in a general case neither the exact nodal structure nor the exact hypernodal structure are known, so it is difficult to assess the relative quality of the two estimates.

In general, a possible strategy for better exploiting the hypernodal functions would be that of optimizing the hypernodal structure (following a variational procedure analogous to that used for standard functions), rather than relying on

the optimization of the antisymmetric functions. Some aspects though, like the correspondence between the FN and FHN results in the case of the Be atom, warrant additional study.

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