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The exchange potential in path integral studies: Analytical justification

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We present analytical justification for our previously described exchange pseudopotential. We show how the fermi quantum partition function can be constructed from the Boltzmann (distinguishable particle) wave functions if the states that correspond to like-spin electrons occupying the same quantum state are excluded. A class of weighting functions that satisfy this constraint approximately is discussed. Our previous pseudopotential falls under this class. Essentially, our pseudopotential forces the unwanted states to have high energy and, hence, to make negligible contribution to the partition function. Exchange potentials of the form discussed in this article should be useful for studying systems where the (allowed) correlated Boltzmann wave functions have negligible amplitude for like-spin fermion-fermion distances less than the diameter of the individual particle wave packets. For example, in the case of two spin-up (or spin-down) fermions, if one fermion is located at r , then $|\Psi(r, q)|^2$ is negligible if $q \cong r$. This should be the case for systems where a tight binding model is appropriate or for systems with strong interparticle repulsions.

I. INTRODUCTION

The study of quantum mechanical many-body systems is of fundamental importance to our understanding of chemistry and physics. Of particular interest in this paper are dense, disordered quantum systems, where traditional quantum techniques are frustrated by the lack of long-range order and the presence of strong intermolecular forces, which hinder the simplification of the many-body Hamiltonian. Quantum mechanics plays a central role in processes ranging from electron solvation dynamics and electron transfer to chemical reaction dynamics and conduction in semiconductors and metals. One of the most successful methods for treating condensed phase quantum systems is the path integral formulation of quantum mechanics,^{1,2} which replaces a quantum Hamiltonian with a classical Hamiltonian upon which classical techniques can be applied. To date, virtually all path integral studies have been limited to systems where Fermi statistics are not important,^{2,3} due in part to the difficulty of treating exchange. Recently, we have used a pseudopotential based approach for treating exchange⁴ and have applied it to an ideal gas of fermions in a harmonic well and to the triplet state of the sodium dimer. Our justification for the form of the pseudopotential was physical in nature and did not address the analytical properties of the approximation. In this paper, we show how our exchange potential is one of a class of pseudopotentials that can be used to study many-fermion systems in which the *correlated* Boltzmann wave functions (from which the antisymmetrized wave functions can be obtained) important in determining the system's properties have negligible overlap between like-spin fermions. Thus, this approach can be used to study systems with many sites at which the *correlated* fermions can be localized (such as electrons in a metal or semiconductor) or even many-electron atoms.

II. REVIEW OF PSEUDOPOTENTIAL APPROACH TO EXCHANGE

In this section, we will briefly review our solution⁴ to the problems associated with using path integrals to study

many-fermion systems. Consider evaluating the partition function for a two fermion Hamiltonian. In the usual discretized path integral formulation we have¹

$$Q = \int dr^P dq^P \prod_{i=1}^P \rho(r_i q_i r_{i+1} q_{i+1}, \beta/P), \quad (2.1)$$

where $\beta = 1/k_B T$ (we will use $\epsilon = \beta/P$), ρ is the density matrix, P is the number of points in the path, and r and q refer to the two different fermions. If the two fermions have opposite spin, they cannot exchange and the path integral evaluation of Q presents no computational difficulty. If, however, the two particles have the same spin,

$$\rho(r_i q_i r_{i+1} q_{i+1}, \epsilon) \propto \langle r_i q_i | e^{-\epsilon \mathcal{H}} | r_{i+1} q_{i+1} \rangle - \langle r_i q_i | e^{-\epsilon \mathcal{H}} | q_{i+1} r_{i+1} \rangle,$$

where \mathcal{H} is the system's Hamiltonian and ρ can be positive or negative depending on the coordinates r_i , q_i , r_{i+1} , and q_{i+1} . In the small ϵ limit, one can show that

$$Q \propto \int dr^P dq^P \prod_{i=1}^P \langle r_i q_i | e^{-\epsilon \mathcal{H}} | r_{i+1} q_{i+1} \rangle \times \{1 - \exp[-(r_i - q_i) \cdot (r_{i+1} - q_{i+1})/\epsilon]\}, \quad (2.2)$$

where in the path integral formulation, $\{r_i\}$ and $\{q_i\}$ represent paths the two quantum particles can take in imaginary time. Since the subscript i refers to a particular imaginary time, the Hamiltonian couples only particles that differ by zero or one unit imaginary time.¹ Our approximate form was arrived at by making what appears to be a mean field approximation:

$$Q \cong \int dr^P dq^P \prod_{i=1}^P \langle r_i q_i | e^{-\epsilon \mathcal{H}} | r_{i+1} q_{i+1} \rangle \times \prod_{j=1}^P \{1 - \exp[-\alpha |r_i - q_i| \cdot (r_j - q_j)/\epsilon]\}^{1/P}. \quad (2.3)$$

Here, α is a Hamiltonian independent constant that was chosen to give the correct results in one system at one temperature, and the absolute value of the dot product prevents neg-

This is just the Boltzmann density matrix in state k . Thus

$$Q \propto \int dr^P dq^P \sum_k' \rho_k^B(r_1 q_1 r_2 q_2 \epsilon) \rho_k^B(r_2 q_2 r_3 q_3 \epsilon) \times \cdots \rho_k^B(r_P q_P r_1 q_1 \epsilon). \quad (3.10)$$

Let the set of states k that contribute to Q be denoted by $\{F\}$ and assume that we can find a function $\tilde{f}(\{r^P\}, \{q^P\})$ such that

$$\int dr_2 dq_2 \rho_k^B(r_1 q_1 r_2 q_2 \epsilon) \rho_j^B(r_2 q_2 r_3 q_3 \epsilon) \tilde{f}(\{r^P\}, \{q^P\}) = 0 \quad \text{if} \quad \begin{cases} k \neq j \\ \text{or} \\ k = j \text{ and } k \notin \{F\} \end{cases}. \quad (3.11)$$

Below, we will discuss the circumstances under which such a function may be found. Given \tilde{f} , we can write Q as

$$Q \propto \int dr^P dq^P \prod_{j=1}^P \left[\sum_k \rho_k^B(r_j q_j r_{j+1} q_{j+1} \epsilon) \right] \times \tilde{f}(\{r^P\}, \{q^P\}). \quad (3.12)$$

$\sum_k \rho_k^B(r_1 q_1 r_2 q_2 \epsilon) = \rho^B(r_1 q_1 r_2 q_2 \epsilon)$ is just the Boltzmann density matrix in the position representation, for which numerous approximations exist. In addition, ρ^B is non-negative and, hence, can be sampled by standard liquid methods. The effects of exchange reside entirely within the sum over k ; \tilde{f} must exclude those states that do not contribute to the fermion partition function. Thus, the fermion partition can be written in terms of the Boltzmann density matrix if an appropriate function \tilde{f} can be found.

We now demonstrate that under certain conditions, Eq. (3.11) can be satisfied approximately. To do this we must show that

$$\int dr_2 dq_2 \phi_k^*(r_2 q_2) \phi_{k'}(r_2 q_2) \tilde{f} \approx 0 \quad (3.13)$$

for $k \neq k'$ or for $k = k' \notin \{F\}$ for some choice of \tilde{f} . Since $\tilde{f} = 1$ would give the proper weighting for $k = k' \in \{F\}$, we want \tilde{f} to deviate from unity only in those regions of space where $\phi_k(r_2 q_2)$ is small for $k \in \{F\}$. If $k \notin \{F\}$, ϕ_k will be symmetric in its coordinates, since otherwise $\phi_k(r_2 q_2) - \phi_k(q_2 r_2) [\propto \Psi_k(r_2 q_2)]$ would not vanish, as required by the Pauli exclusion principle. Thus, if ϕ is expanded in a complete set of single particle eigenstates, it must have the form

$$\phi_k(r_2 q_2) = \sum_{\alpha} a_{\alpha}^k \chi_{\alpha}(r_2) \chi_{\alpha}(q_2). \quad (3.14)$$

On the other hand, $\phi_k \in \{F\}$ has the form

$$\phi_k(r_2 q_2) = \sum_{\alpha, \beta} a_{\alpha\beta}^k \chi_{\alpha}(r_2) \chi_{\beta}(q_2). \quad (3.15)$$

Note that $a_{\alpha\beta}^k$ is not a symmetric function. Assume that ϕ_k can be adequately represented by a set $\{\chi\}$ of localized functions; that is, the states $\{\chi\}$ have significant amplitude only in a small region of space ($\{\chi\}$ should be thought of as molecular orbitals, rather than atomic orbitals). This assumption will be valid in a variety of systems, from chemical bonds to metals, where the conduction electrons can be studied using a tight-binding model. The largest contributions of

$\phi_k \notin \{F\}$ to Eq. (3.13) will come when $|r_2 - q_2| < \Delta$, the size of the single particle wave packets. On the other hand, there is no *a priori* reason for $\phi_k \in \{F\}$ to have finite amplitude as r_2 approaches q_2 . If $\{\chi\}$ are localized on different spatial sites, then we expect $\phi_k(r_2 q_2)$ $k \in \{F\}$ to be negligible as $r \rightarrow q$. If some of the functions χ are located at the same spatial site (such as might occur in an atomic calculation), this does not mean that ϕ is large as $r_2 \rightarrow q_2$, since ϕ is the correlated wave function. Indeed, it is well known that the diagonal component of the two particle density $\rho^2(r_1, r_1)$ is about half the bulk density, due to the exclusion of the like-spin electrons (which make up roughly half the total electrons). Thus, if Δ is small compared to the average distances between like-spin particles for $\phi_k \in \{F\}$, we can categorize the Boltzmann wave functions ϕ_k according to their behavior as r_2 approaches q_2 ; states that should be excluded from the fermion partition function will have a major contribution in regions where $|r_2 - q_2| < \Delta$, while states that contribute to the partition function will have a small contribution from regions where $|r_2 - q_2| < \Delta$. Thus, \tilde{f} can differ from unity in regions of small interparticle distances without affecting significantly the contributions from states $\phi_k \in \{F\}$. Our strategy is to pick \tilde{f} to go to zero as $r \rightarrow q$ and to approach unity as $|r_2 - q_2| \rightarrow \infty$. This will ensure the proper weighting for large like-spin particle distances and make negligible the contribution from ϕ_k , $k \notin \{F\}$ to the partition function. In addition, different states will not be connected by \tilde{f} , since regions in phase space that are important for $k, k' \in \{F\}$ are weighted with unit weight (approximately) and hence, the orthogonality constraint should still hold (if either or both of k and $k' \notin \{F\}$, $\tilde{f} \approx 0$ in the regions where the wave functions are large and, hence, integrations over phase space will give 0). Thus, while this may not completely exclude the undesired contributions to Q , it will make them very small compared to the desired contributions. Another way of putting this is that we are increasing the energy of the forbidden states and, hence, they are no longer important in determining the system's properties (since their contributions are $\propto e^{-\beta E}$). The same situation occurs in the usual pseudopotential theory, where the core energy levels are shifted to very high energies. This also occurs in the practical applications of density functional theories, where, due to the approximate treatment of exchange and correlation, the Pauli exclusion principle is not satisfied since the energy of two like-spin particles in the same orbital is not infinity, but is some large number. This forces the system into the lower energy triplet state in an analogous manner to our path integral procedure. Thus, if \tilde{f} with the above properties can be found, we should be able to obtain accurate results for many-fermion systems.

How should we go about developing a function \tilde{f} ? It is clear from our previous work⁴ that setting

$$\tilde{f} = \prod_{j=1}^P \prod_{k=1}^P \{1 - \exp[-\alpha |(r_k - q_k) \cdot (r_j - q_j)|/\epsilon]\}^{1/P} \quad (3.16)$$

gives excellent agreement with exact results. We now demonstrate that Eq. (3.16) is a reasonable guess for function \tilde{f} . Equation (3.5) shows that the fermion density matrix will

differ from the Boltzmann density matrix by terms like $|1 - \phi_k(q, r)/\phi_k(r, q)|^2$ for each k . Notice that this term is identically zero for $k \notin \{F\}$. Thus, we need an approximation to ϕ_k . While this means that in principle \tilde{f} is k dependent, we will show how the short time propagator in the position representation allows us to estimate the wavefunction ϕ_k from the set of positions $\{r^P\}, \{q^P\}$.

Consider the weight associated with a single quantum particle in a fixed quantum state:

$$\rho_j(r_1 r_2 \epsilon) \rho_j(r_2 r_3 \epsilon) \cdots \rho_j(r_P r_1 \epsilon) = e^{-\beta E_j} |\phi_j(r_1)|^2 |\phi_j(r_2)|^2 \cdots |\phi_j(r_P)|^2. \quad (3.17)$$

In the short-time approximation this has the form

$$\rho_j(r_1 r_2 \epsilon) \rho_j(r_2 r_3 \epsilon) \cdots \rho_j(r_P r_1 \epsilon) \propto \exp \left[-P/2\beta \sum_{i=1}^P (r_i - r_{i+1})^2 - \beta/P \sum_{i=1}^P V(r_i) \right] \quad (3.18)$$

and

$$E_j = 3P/2\beta - P/2\beta^2 \sum_{i=1}^P (r_i - r_{i+1})^2 + 1/P \sum_{i=1}^P V(r_i), \quad (3.19)$$

where $V(r_i)$ is the potential energy. This means that the short-time approximation for the wave functions is Gaussian, but in a different sense than one usually means. Each particle is harmonically bound to another point in the path, rather than to a center. Since there is no connection between r_i and r_{i+1} in Eq. (3.17) when the system is in a pure state, we can connect r_i to any other particle. Since the wave packets are Gaussian, we find

$$\begin{aligned} 1 - \phi_k(q, r)/\phi_k(r, q) &= 1 - \exp[-\lambda(q - R)^2 - \lambda(r - Q)^2]/ \\ &\quad \exp[-\lambda(r - R)^2 - \lambda(q - Q)^2] \\ &= 1 - \exp[-2\lambda(r - q) \cdot (R - Q)], \end{aligned} \quad (3.20)$$

where λ is related to the eigenvalue of ϕ_k and $R(Q)$ can refer to any of the beads $\{r_i\}$ ($\{q_i\}$). To make the above equation go to 1 as $|r - q| \rightarrow \infty$, we must take the absolute value of the dot product. Since R and Q can correspond to any of the other coordinates, we use the "average"

$$\tilde{f} = \prod_{i,j} \{1 - \exp[-2\lambda |r_i - q_i| \cdot (r_j - q_j)]\}^{1/P}. \quad (3.21)$$

The average must be a geometric average to preserve the Pauli exclusion principle. Notice that \tilde{f} will only be small if $\{r_i - q_i\}$ is small for most i ; this is just the behavior we expect from ϕ_k , $k \notin \{F\}$.

We must now estimate λ . We can do this from the properties of the short-time propagator. Consider the short-time propagator for a single quantum particle. This given by $\rho(r, r', \epsilon) = \langle r | e^{-\epsilon \mathcal{H}} | r' \rangle$, where $\epsilon = \beta/P$. It is well known that if the short-time approximation is valid, $\rho(r, r', \epsilon) \cong 0$ unless $r \cong r'$.¹ Thus, $\rho(r, r', \epsilon) \cong \delta(r - r')$ for ϵ small. Expanding ρ in the eigenfunctions of the Hamiltonian, we find

$$\rho(r, r', \epsilon) = \sum_k \psi_k^*(r) e^{-\epsilon E_k} \psi_k(r'). \quad (3.22)$$

We also know that

$$\delta(r - r') = \sum_k \psi_k^*(r) \psi_k(r'). \quad (3.23)$$

Examination of Eqs. (3.22) and (3.23) indicates that ϵ must be small enough so that $\exp(-\epsilon E_k)$ is a slowly varying function of k . Thus, $\epsilon E_k \cong \epsilon \lambda \cong \alpha/2$, where $\alpha/2 < 1$. Substituting this into Eq. (3.21) leads to

$$\tilde{f} = \prod_{i,j} \{1 - \exp[-\alpha |r_i - q_i| \cdot (r_j - q_j)/\epsilon]\}^{1/P} \quad (3.24)$$

which is the same as our previous work. Our previous work⁴ used $\alpha = 0.6$, which is consistent with our estimate.

We now examine Eq. (3.24) in some detail. Let z denote α times the absolute value of the dot product and note that for finite ϵ , $\tilde{f}(z/\epsilon) \rightarrow 0$ as $z \rightarrow 0$ and $\tilde{f}(z/\epsilon) \rightarrow 1$ as $z \rightarrow \infty$. In addition, \tilde{f} has the behavior as a function of ϵ shown in Fig. 1. That is, as $\epsilon \rightarrow 0$ (the limit we take when we discretize the path integral), \tilde{f} is unity over larger regions of r_2 and q_2 if z is finite. If $z \neq 0$, then

$$\begin{aligned} \tilde{f}(z/\epsilon) &= \tilde{f}|_{\epsilon=0} - \epsilon \left[\frac{z}{\epsilon^2} \cdot \frac{\partial \tilde{f}}{\partial (z/\epsilon)} \right] |_{\epsilon=0} + O(\epsilon^2) \\ &= 1 - \epsilon \left[\frac{z}{\epsilon^2} \cdot \frac{\partial \tilde{f}}{\partial (z/\epsilon)} \right] |_{\epsilon=0} + O(\epsilon^2). \end{aligned} \quad (3.25)$$

If the term in brackets is zero for $\epsilon = 0$ (as it is in our approximation), \tilde{f} will not connect different states and will properly weight the states $k \in \{F\}$ to order ϵ , which is the accuracy of the usual short time approximation.¹ Thus, as long as z is finite in those regions of phase space that contribute significantly to Eq. (3.11), \tilde{f} will not connect different states and will weight correctly the regions of phase space.

The dot product z can go to zero either as the length of one of the two vectors approaches zero or as the angle between them goes to 90° . For systems with repulsive interactions or with spatially separated fermion binding sites, we expect that the regions of phase space that contribute to Eq. (3.11) have relatively large values of $|r_1 - q_1|$ and $|r_2 - q_2|$ for $k \in \{F\}$, since $\phi_k(r, q)$ is the *correlated* wave function and should have vanishingly small amplitude as r

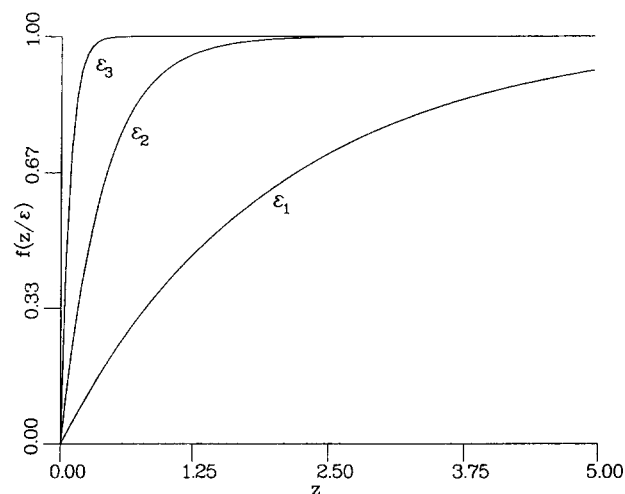


FIG. 1. Plot of $f(z/\epsilon)$ vs z for three values of ϵ . As $z \rightarrow \infty$, $f \rightarrow 1$. The z axis has arbitrary units and $\epsilon_1 > \epsilon_2 > \epsilon_3$.

approaches q (for particles with the same spin, which we are considering). For $k \notin \{F\}$, $z = 0$ is the important region of the integration space. In this region, $\tilde{f} = 0$, as we desire.

A more serious constraint is that the angle between the vectors not approach 90° . To examine this constraint, imagine a small region in space in which $\int dq \phi_k(r, q)$ is significant. Now find the corresponding set of q values for which $\phi_k(r, q)$ is large. We can imagine two limiting cases, as shown in Fig. 2. The first is where there is negligible overlap between the set of r values and the set of q values. In this case we can estimate the minimum value of $\cos \gamma$, where γ is the angle between the two vectors. If x is the radius of the two regions and D is the distance between the two regions, $\cos \gamma = 1 - 2x^2/(x^2 + D^2/4)$. If $D > x$, this number will certainly be greater than 0 and, hence, will remain finite even as $\epsilon \rightarrow 0$. $D > x$ will occur when states are localized at different points in space or when the interparticle interactions are strongly repulsive (as will happen for electrons). We should emphasize that the relative magnitudes of x and D are properties of the *correlated* wave functions and, consequently, $D > x$ can occur even when the particles are centered about the same site in space. That is, while the molecular orbitals that are determined from a Hartree-Fock calculation may indicate significant overlap between particles, the correlated wave functions that result from a configuration-interaction (CI) calculation may indeed satisfy $D > x$. Thus, the approximate form used above may work even for many-electron atoms. Indeed, the success of the method in treating

noninteracting fermions localized about a single point in space (three-dimensional harmonic oscillator) indicates this to be the case.

The other case we need to consider occurs when $D < x$. In this case, there are potentially many sets of (r, q) for which the dot product is small. Even here, though, Eq. (3.11) may still be satisfied. If we hold $\cos \gamma$ fixed and vary $|r_2 - q_2|$ ($\equiv X$), there will be a certain range of X values for which \tilde{f} is approximately constant since $|(r_1 - q_1) \cdot (r_2 - q_2)|/\epsilon \ll 1$. If it so happens that the wave functions are orthogonal when the integrations are performed in this manner, then Eq. (3.11) will still be satisfied. In addition, there may be symmetry considerations that lead to orthogonality. Thus, even in this rather extreme limit of overlap (which may not be of importance in chemical systems), Eq. (3.11) may hold.

IV. DISCUSSION

We have shown how an approximate exchange potential can be used in path integral studies. Under the conditions of small overlap between particles (with like-spin) in the correlated wave functions, approximate pseudopotentials of the type shown above adequately represent exchange. It should also be emphasized that our approximation does not require a "guess" other than that like-spin particles have small overlap in the correlated Boltzmann wave function. In contrast, most of the other quantum techniques that are used to study disordered many-fermion systems require much more information about the wave functions. These other methods include both the traditional quantum techniques (HF, CI, etc.) and the so-called "quantum Monte Carlo methods" (Green's function and diffusion Monte Carlo,⁵ for instance). In addition, our method has a reasonably well defined limit of validity, in contrast to density functional methods⁶ which rely on a local density approximation to both exchange and correlation. Finally, path integral techniques are useful because temperature is included, allowing for transitions between electronic states; this ability is either absent or difficult to include in the aforementioned approaches.

In our simulations, we have used the "primitive" estimator for ρ^B , along with Eq. (3.16). It is possible to use higher quality estimates for either ρ^B and \tilde{f} , if they exist. We can also imagine using the wave functions determined from these calculations as inputs into other quantum chemical methods, particularly those that require an initial guess for the wave function such as Green's function Monte Carlo or diffusion Monte Carlo. It will also be worthwhile to investigate the possibility of using functions of the form \tilde{f} in density functional calculations in the place of exchange terms or to evaluate the exchange-correlation hole. Finally, it will be important to determine the limits of the method by examining many-electron atoms and systems with unbound electrons.

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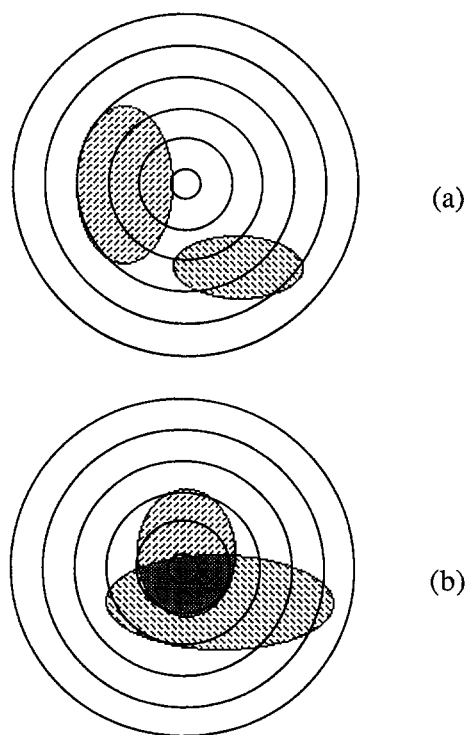


FIG. 2. Representations of two possible correlated wave functions. The concentric circles denote regions where $|\psi(r, q)|^2$ is large for some values of r and q . Given that r is in one of the shaded regions, the other shaded region denotes that set of q for which the wave function has significant amplitude. (a) There is no amplitude for $r \approx q$. (b) There is a region of overlap, here indicated by the dark shaded region.

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