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Finite-temperature electronic simulations without the Born-Oppenheimer constraint

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The adiabatic approximation, typically assumed when performing standard Born-Oppenheimer (BO) molecular dynamics, can become unreliable at finite temperature, and specifically when the temperature is larger than the electronic energy gap between the ground state and the low-lying excited states. In this regime, relevant for many important chemical processes, the non-adiabatic couplings between the electronic energy states can produce finite temperature effects in several molecular properties, such as the geometry, the vibrational frequencies, the binding energy, and several chemical reactions. In this work, we introduce a novel finite-temperature non-adiabatic molecular dynamics based on a novel covariant formulation of the electronic partition function. In this framework, the nuclei are not constrained to move in a specific electronic potential energy surface. Then, by using a rigorous variational upper bound to the free energy, we are led to an approximate partition function that can be evaluated numerically. The method can be applied to any technique capable to provide an energy value over a given wave function ansatz depending on several variational parameters and atomic positions. In this work, we have applied the proposed method within a quantum Monte Carlo (QMC) scheme. In particular, we consider in this first application only classical ions, but we explicitly include an electronic correlation (Jastrow) term in the wave function, by extending in this way the standard variational QMC method, from ground state to finite temperature properties. We show that our approximation reduces correctly to the standard ground-state Born-Oppenheimer (gsBO) at zero temperature and to the correct high temperature limit. Moreover, at temperatures large enough, this method improves the upper bound of the free energy obtained with a single BO energy surface, since within our approach it is possible to estimate the electron entropy of a correlated ansatz in an efficient way. We test this new method on the simple hydrogen molecule, where at low temperature we recover the correct gsBO low temperature limit. Moreover, we show that the dissociation of the molecule is possible at a temperature much smaller than the one corresponding to the gsBO energy surface, in good agreement with experimental evidence. Several extensions of the proposed technique are also discussed, as for instance the inclusion of quantum effects for ions and the calculation of critical (magnetic, superconducting) temperatures. [http://dx.doi.org/10.1063/1.4755992]

I. INTRODUCTION

The calculation of finite temperature properties is one of the most important and challenging aspects of the numerical simulations. The basis of most finite temperature computational approaches is the Born-Oppenheimer (BO) separation of the system in the electronic and nuclear subsystems, implying that at zero temperature the nuclei move in a potential energy surface (PES) provided by the electrons. This approximation is justified by the large difference between the electronic mass m_e and the average nuclear mass M, as demonstrated in the seminal paper of BO[1] by expanding perturbatively the Schrödinger equation in terms of $(m_e/M)^{1/4}$.

Moreover, when studying systems at non zero temperatures, it is a common practice to consider electrons in their instantaneous ground state, while the nuclei can be treated as classical particles following an *ab initio* finite temperature molecular dynamics. The equilibrium properties are then calculated by computing time averages over long enough molecular dynamics trajectories. This is for instance the case of the ground-state Born-Oppenheimer (gsBO) molecular dynamics and of other equivalent approaches such as the Car-Parrinello molecular dynamics.[2] These methods also implicitly use an adiabatic approximation, because the BO approximation does not provide only one PES, but several adiabatic potential energy surfaces, one for each electronic eigenstate. However, the nuclei are evolved only according to one adiabatic PES and the non-adiabatic coupling between adiabatic PESs is neglected. This approximation is reliable only if the electronic energy gap is large, namely, when the gap between the electronic ground state and the low-lying excited states is much larger than the thermal energy. If the temperature is high enough this is not the case, and it is not correct to assume

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that the electrons are constrained into one adiabatic PES. This happens also at room temperature in many chemical processes, and effects can be observed in several molecular properties, such as the geometry, the vibrational frequencies, the binding energy, and several chemical reactions.[3] Moreover, these effects can also be important in many physical phenomena, such as the occurrence of magnetic or insulating phases below a critical temperature, where the electronic entropy cannot be neglected.

In the past several progresses have been done by extending the density functional theory (DFT) method to finite temperature[4,5] by working with fractional occupation numbers, or by using quantum Monte Carlo[6] (QMC) within various path integral formulations,[7–12] especially in the study of the hydrogen phase diagram.[13–20] In both cases, many problems remain as, for instance, the lack of an accurate local functional at finite temperature for DFT methods[21–23] does not allow the same degree of accuracy of the corresponding zero temperature DFT functionals, and, within QMC techniques, it is difficult to deal with the fermion sign problem.[24] For the above reasons, both methods have not been spread to a wide spectrum of applications. In this paper, we aim to account for the possibility of electronic excitations by removing the adiabatic constraint forcing the electrons to remain, during the dynamics, only in a specific PES. This is particularly important for QMC methods as, due to the statistical noise, it is extremely difficult to satisfy exactly the BO constraint.

Following the BO derivation, by using the smallness of the ratio m_e/M, the total partition function Z can be expressed in terms of an electronic partition function $Z[\mathbf{R}]$ at fixed nuclei positions,

$$Z = \int d\mathbf{R} Z[\mathbf{R}], \tag{1}$$

$$Z[\mathbf{R}] = \mathrm{Tr} \exp(-H_{\mathbf{R}}/T), \tag{2}$$

where T is the temperature (here and henceforth the Boltzman constant is assumed to be one and we neglect for simplicity the overall constant coming from integration of the atomic momenta), $H_{\mathbf{R}}$ is the standard electronic Hamiltonian, that includes also the classical ionic contribution, and that depends only parametrically upon the atomic positions $\mathbf{R}$. As previously discussed, we remark that we are assuming here that the temperature is high enough that quantum effects on heavy nuclei can be neglected, so that it is justified to have taken the classical limit for the nuclei. Observe that, within the standard BO approach, whenever the electronic gap is much larger than T, the electronic partition function $Z[\mathbf{R}]$ in (2) can be approximated by $\exp(-E_0(\mathbf{R})/T)$, where $E_0(\mathbf{R})$ is the ground state energy of the Hamiltonian $H_{\mathbf{R}}$; in other words, a single adiabatic PES is implicitly considered in this case.

In the following derivation, we want to include the contribution of all the adiabatic PESs corresponding to the ground state and all excited states with an affordable computation, because, as emphasized before, considering only the electronic ground-state PES (gsPES) may fail in several cases, even when we are in the limit of small m_e/M. For instance, the occurrence of a broken symmetry phase often implies gapless electronic excitations in $H_{\mathbf{R}}$, and the approximation $Z[\mathbf{R}] \sim \exp(-E_0(\mathbf{R})/T)$ cannot be safely assumed. Other examples are conical intersections,[25–27] when, for some particular ionic positions, $H_{\mathbf{R}}$ becomes gapless and nearby, the proximity between different (namely, corresponding to low-lying excited states) PES is possible. In these conditions, a pure electronic ground state technique fails as the interplay between different adiabatic energy surfaces cannot be taken into account consistently.

We are able to achieve the main task of this paper within a rigorous variational upper bound of the total free energy $F = -T \ln Z$. The method we propose is supposed to be simple enough to avoid most of the known drawbacks, as it does not rely on the knowledge of any particular functional, or, within our variational approximations, can be employed by QMC, without facing the so called "fermion sign problem."

The paper is organized as follows. The derivation of the approximate expression of the electronic partition function introduced and used in this work is given in Sec. II, and some important but more detailed aspects are reported in Appendixes A–D. This derivation is not specific for a QMC framework, indeed Appendix D is specifically oriented to an implementation of the method into a Hartree-Fock or DFT framework. Next, we show how to sample the introduced partition function using a Langevin dynamics for the wave function parameters in Sec. III, and the ion coordinates in Sec. IV. In Sec. V, we finally show some results we have obtained using this approach for the hydrogen molecule.

II. FINITE TEMPERATURE ELECTRONIC PARTITION FUNCTION

We consider the problem to estimate the finite temperature partition function of an electronic system with N electrons and M atoms, where we assume in the following that, as discussed in the introduction, the ions are classical particles, whose coordinates $\mathbf{R}$ appear just as simple parameters in the electronic Hamiltonian $H_{\mathbf{R}}$ and are confined in a finite volume V. Therefore, once the ion positions are fixed, we need to evaluate the electronic partition function,

$$Z[\mathbf{R}] = \mathrm{Tr} \exp(-\beta H_{\mathbf{R}}), \tag{3}$$

where $\beta = 1/T$. Our derivation applies for the Hamiltonian with a bounded spectrum defined in a finite Hilbert space with dimension D. Generally speaking, this is not a relevant restriction as, for instance, in electronic structure calculation one can consider a finite dimensional basis of localized orbitals around each atom. The basis and the dimension D can be increased arbitrarily to reach the so called complete basis set limit, that describes a proper continuous electronic system.

In order to simplify the notations, we can consider standard creation operators with canonical commutation rules, spanning the finite single electron basis, as for a standard lattice Hamiltonian, namely, $c_i^\dagger$ for $i = 1, \ldots, L$, where for shorthand notations i labels also the spin, namely, $i \leq L/2$ ($i > L/2$) refers to spin up(down)-states. We consider the generic wave

function $|\psi\rangle = J \times |SD\rangle$ for a system of N electrons, where

$$J = \exp\left(1/2 \sum_{i,j} v_{i,j} n_i n_j\right), \tag{4}$$

$$|SD\rangle = \left[\prod_{i=1}^{N} \sum_{j=1}^{L} \psi_j^i c_j^\dagger\right] |0\rangle, \tag{5}$$

with $n_i = c_i^\dagger c_i$, $|0\rangle$ is the electron vacuum state, and $v_{i,j}$, ψ_j^i being expansion coefficients over this basis. In the continuous limit, this wave function is the standard Jastrow-Slater one used in QMC in order to describe electron correlation.[28] Extensions of this wave function are possible using the antisymmetrized geminal power (AGP),[29] Pfaffian,[30] backflow,[31] and the following considerations apply also for these more recent ansatz, because they all contain the Slater determinant $|SD\rangle$ in a particular limit. The use of these correlated wave functions has been proved useful also to describe excitations in several molecular systems,[32] excitons in bilayer electronic systems,[33] and recently has been extended also to time-dependent quantum dynamics.[34] It is clear that an accurate description of the excited states, apparently possible with these correlated ansatz, is particularly important for a realistic finite temperature method.

In all cases, the real variational parameters, that define the above wave function, namely, $v_{i,j}$ and ψ_j^i are compactly denoted by $\alpha \equiv \{\alpha_i\}_{i=1,\ldots,p}$ and, since all physical quantities do not depend on the norm of the wave function, we consider the α-manifold of states,

$$|\alpha\rangle = \frac{|\psi\rangle}{\||\psi\rangle\|}. \tag{6}$$

The metric in this manifold becomes non trivial as, by a straightforward calculation, the distance between two states $|\alpha\rangle$ and $|\alpha + d\alpha\rangle$ is given by

$$ds^2 = \||\alpha + d\alpha\rangle - |\alpha\rangle\|^2 = d\alpha^i d\alpha^j S_{i,j}, \tag{7}$$

where summation over repeated indices is assumed, and S is a $p \times p$ matrix defining the metric tensor of this rather non trivial space, described by p independent variational parameters (e.g., a subset of $v_{i,j}$ and ψ_{ij}). The matrix S can be explicitly evaluated and depends only on average first derivatives of the wave function with respect to the parameters $\alpha's$,

$$S_{i,j} = \frac{\langle \partial_i \psi | \partial_j \psi\rangle}{\langle \psi | \psi\rangle} - \frac{\langle \partial_i \psi | \psi\rangle}{\langle \psi | \psi\rangle} \frac{\langle \psi | \partial_j \psi\rangle}{\langle \psi | \psi\rangle}. \tag{8}$$

It defines a metric as it is strictly positive definite if all p variational parameters are independent (implying indeed a non vanishing determinant $|S| > 0$). This matrix turns out to be exactly the one used in several optimization techniques,[35,36] and can be computed also for correlated systems by sampling the correlations of the quantities $O_j(x) = \frac{\langle x|\partial_j \psi\rangle}{\langle x|\psi\rangle}$ over the configuration space $\{x\}$ where electrons have definite spin and position, namely,

$$S_{i,j} = \langle O_i O_j\rangle - \langle O_i\rangle\langle O_j\rangle, \tag{9}$$

where the symbol $\langle \ldots \rangle$ denotes average over a distribution $\Pi(x) \propto \langle x|\psi\rangle^2$, that can be sampled by standard variational Monte Carlo.

In Eq. (3), we use a simple relation for recasting the trace in a finite dimensional Hilbert space as an integral of normalized wave functions $|c\rangle = \sum_{i=1}^{D} x_i |i\rangle$, namely,

$$D \int dx^D \delta(\|x\| - 1) \langle c| \exp(-\beta H) |c\rangle = S_D \mathrm{Tr} \exp(-\beta H), \tag{10}$$

where $S_D = 2\pi^{D/2}/\Gamma(D/2)$ is the area of the D-dimensional unit sphere. The above relation can be immediately proved by substituting $|c\rangle = \sum_{i=1}^{D} x_i |i\rangle$ in the LHS of the above equation and noticing that $\int dx^D \delta(\|x\| - 1) x_i x_j = \delta_{i,j} \int dx^D \delta(\|x\| - 1) x_i^2$, namely, it is non zero only for $i = j$. Then, we can sum the integrand over the dummy index i and divide by D, and obtain $\int dx^D \delta(\|x\| - 1) x_i x_j = \frac{\delta_{i,j}}{D} S_D$, that easily proves Eq. (10), as previously stated.

We note that the simple relation (10) can be used to establish, within a rigorous mathematical framework, the finite temperature Lanczos method used in Ref. 37. In this technique, finite temperature estimates of the partition function are obtained with a finite set of randomly generated states $|c\rangle$, once it is assumed that $\langle c|\exp(-\beta H)|c\rangle$ can be computed with high accuracy with the Lanczos method. Indeed, this is nothing but evaluating statistically the integral in the LHS of Eq. (10), and one does not need any further assumption to validate the method.

The simple relation (10) can be also extended in the space α with non trivial metric, by using the invariant measure $d\alpha^p \sqrt{|S|}$, corresponding to the metric tensor S,

$$\frac{\int d\alpha^p \sqrt{|S|} \langle \alpha| \exp(-\beta H_{\mathbf{R}}) |\alpha\rangle}{Z_S} = \mathrm{Tr} \exp(-\beta H_{\mathbf{R}}), \tag{11}$$

where here and henceforth the symbol $|S|$ indicates the determinant of the matrix S. This relation is proven in Appendix A, provided the dimension of the space is large enough, namely, contains at least the full space of Slater determinant wave functions, where the overall constant has been obtained by using that $Z[\mathbf{R}] = D$ for $\beta = 0$, as the metric normalization Z_S is defined as $Z_S = \frac{\int d\alpha^p \sqrt{|S|}}{D}$. We emphasize here that the relation (11) is *exact* even when the dimension of the space p is much smaller than the dimension of the Hilbert space. For instance, for real Slater determinants, the number $p < NL$ as they are defined by N orbitals each depending on L coefficients (see Eq. (4)), whereas the Hilbert space dimension D grows exponentially with L and N (See Appendix D for the parametrization of an arbitrary real Slater determinant).

In practice, the number p of variational parameters defining the wave function ansatz can be much smaller than that necessary to span all possible Slater determinants. In the case $p \ll NL$, we expect that Eq. (11) is still valid but the trace in the RHS is limited to the largest subspace with dimension D_s spanned by the variational ansatz. Moreover, a weak dependence on R in Z_S is also expected when a basis dependent on the atomic positions is used (it is not the case for a plane wave basis for instance). The calculation can be meaningful also in this case after a careful study of the dependence of the results upon the dimension of the basis chosen, as a common practice in quantum chemistry calculations. In fact, in the limiting case when the one particle basis set used to define the orbitals in the Slater determinant becomes complete the metric

normalization Z_S is independent of R, because any change of basis is equivalent in this limit to a mapping $\alpha \to \alpha'$. Thus Z_S, being explicitly covariant (i.e., its form remains unchanged after any transformation $\alpha \to \alpha'$), is independent of R and can be considered as an irrelevant constant.

Therefore, within the completeness assumption, following the simple derivation of Appendix B, we can easily bound the exact electronic partition function $Z[\mathbf{R}]$, because, due to the convexity of the exponential function, the expectation value of an exponential operator over a normalized state $|\alpha\rangle$ satisfies

$$\langle\alpha|\exp(-\beta H_{\mathbf{R}})|\alpha\rangle \geq \exp(-\beta\langle\alpha|H_{\mathbf{R}}|\alpha\rangle).$$

This immediately provides a rigorous lower bound Z_Q for the partition function Z,

$$Z \geq Z_Q = \frac{\int d\mathbf{R}\int d\alpha^p \sqrt{|S|}\exp(-\beta\langle\alpha|H_{\mathbf{R}}|\alpha\rangle)}{Z_S}, \tag{12}$$

and a corresponding upper bound F_Q for the free energy $F = -T\ln Z$,

$$F \leq F_Q = -T\ln Z_Q. \tag{13}$$

In this way, it is evident that F_Q represents an improvement to the standard practice to consider only the lowest BO energy surface. In fact, in this approximation only one state is assumed to contribute to the integral in Eq. (12), namely, the lowest energy state of $H_{\mathbf{R}}$ within the ansatz given by $|\alpha\rangle$,

$$E_{BO}[\mathbf{R}] = \min_{\alpha}\{\langle\alpha|H_{\mathbf{R}}|\alpha\rangle\}. \tag{14}$$

Indeed, it is clear that $F = \min_{\mathbf{R}}\{E_{BO}[\mathbf{R}]\}$ only at $T = 0$, and it represents a very bad approximation to F as long as the temperature is raised, whereas the approximate partition function F_Q approaches the correct large temperature limit $-T\ln(DV^M)$ of the exact partition function, while remaining a rigorous upper bound for any T.

In Appendix C, we see in detail a comparison between the approximated partition function Z_Q here introduced, with the exact and gsBO ones, showing that our approximation turns out to be better than the gsBO one, above a temperature T^*, that remains meaningful in the thermodynamic limit.

III. MONTE CARLO SAMPLING OF THE PARTITION FUNCTION Z_Q

In principle, the partition function Z_Q can be sampled by almost standard Monte Carlo methods, whenever the metric S and the expectation value of the energy H over the ansatz $|\alpha\rangle$ are known, for instance within the Hartree-Fock theory, namely, when $|\alpha\rangle$ represents just a simple Slater determinant. It is also possible to replace in Z_Q the expectation value of the energy with any DFT functional depending on $|\alpha\rangle$, through the corresponding density or gradient, the condition of functional minimum being recovered correctly at $T = 0$. For a discussion about the space of parameters for a Slater determinant wave function, and the introduction of an invariant measure in this space, see Appendix D.

However, in the truly correlated case, namely, when the ansatz $|\alpha\rangle$ differs from a Slater determinant, there are extra complications because both the matrix S and $\langle\alpha|H_{\mathbf{R}}|\alpha\rangle$ are known only within statistical accuracy. In this case, a possible way to sample the partition function Z_Q and the corresponding thermodynamic quantities is to use the penalty method,[38] introduced some years ago, by using a cost function,

$$V_P(\alpha, \mathbf{R}) = \langle\alpha|H_{\mathbf{R}}|\alpha\rangle - \frac{1}{2\beta}\ln|S|, \tag{15}$$

that can be computed statistically with corresponding error bars.

In the following, we have chosen a different route by employing a finite temperature molecular dynamics rather than the Monte Carlo sampling, because recent QMC packages provide efficient estimates of energy derivatives and ionic forces.[39,40]

Our goal is to sample points in the electronic parameter space α distributed according to the probability distribution defined in Eq. (12), by using first order derivatives of the cost function. In the standard Cartesian metric, it is possible to use a Langevin dynamics for the variables $\{\alpha\}$ and $\{\mathbf{R}\}$, by means of the standard first order equation of motions,

$$\dot{\vec{x}} = -\partial_{\vec{x}}V + \vec{\eta}, \tag{16}$$

where $\vec{x}$ is a covariant vector in a finite dimensional euclidean space, whereas $\partial_{\vec{x}}V(x)$ is the derivative (force) of a potential V. By means of this equation, it is well known that it is possible to sample the equilibrium distribution $W_{eq}(x) = \exp(-\beta V(x))$ provided we satisfy the fluctuation dissipation theorem, implying that

$$\langle\eta_i(t)\eta_j(t')\rangle = \delta(t-t')\delta_{i,j}\frac{2}{\beta}. \tag{17}$$

Now, we suppose to change the reference coordinate system by means of a generic transformation of variables $x \to \alpha$ (a p-dimensional non linear mapping as in general relativity). In the following, we have to take into account the Jacobian of such mapping, denoted in the following by the matrix L:

$$L_{i,j} = \partial_{x_j}\alpha_i(\vec{x}). \tag{18}$$

Then, the Langevin equation in this new reference can be easily obtained

$$\dot{\vec{\alpha}} = -S^{-1}\frac{\partial V}{\partial\vec{\alpha}} + L\vec{\eta}, \tag{19}$$

where $S^{-1} = LL^{\dagger}$, and Eq. (17) that defines the fluctuation dissipation theorem remains unchanged.

Equation (19) is covariant if we just replace the matrix S with the matrix defining the metric in a generic curved space

$$ds^2 = S_{i,j}d\alpha_i d\alpha_j, \tag{20}$$

where in this formalism sums over repeated indices are conventionally assumed. Indeed, after the given transformation the above metric tensor transforms as

$$S \to (L^{\dagger})^{-1}SL^{-1} \tag{21}$$

that leaves unchanged the covariant first order Langevin equation (19), as expected.

Thus, from the above equation, we obtain the desired result with the matrix L given by any solution of the matrix

equation,

$$S^{-1} = LL^{\dagger}.$$

Unfortunately, Eq. (19) looks a bit complicated when it is discretized in times $t_n = \Delta n$, because the integral of the random noise depends explicitly on the curvature of the non linear space by means of the matrix L, and the resulting integration is not univocally defined, simply because the solution $S^{-1} = LL^{\dagger}$ is not unique. Indeed, S^{-1} remains unchanged under the substitution $L \to LU$, where U is an arbitrary unitary matrix. In order to remove this arbitrariness, according to Risken,[41] we can work out the integral of the equation of motion in a small time interval of length Δ, by requiring also that the corresponding Markov process

$$\begin{aligned}\alpha(t_{n+1})^i &= \alpha(t_n)^i - \Delta\left[S^{-1}(t_n)\partial_{\vec{\alpha}}\left(V - \frac{1}{2\beta}\ln|S|\right)(t_n)\right]^i \\ &\quad + \frac{1}{2}\sum_k \partial_{\alpha_k} D_{i,k} + y_n^i, \\ \left\langle y_n^i y_n^j\right\rangle &= D_{i,j} = \frac{2\Delta}{\beta} S^{-1}_{i,j}(t_n)\end{aligned} \tag{22}$$

has the correct equilibrium distribution for $\Delta \to 0$:

$$W_{eq}(\alpha) \propto \sqrt{|S(\alpha)|}\exp(-\beta V(\alpha)). \tag{23}$$

In fact, it is possible to show that, only with the above definition of the drift term, the associated and univocally defined Fokker-Planck equation for the probability distribution $W(\alpha, t)$ reads for $\Delta \to 0$:

$$\begin{aligned}\partial_t W(\alpha, t) = \sum_j \partial_j \Bigg\{ &\sum_i \frac{1}{\beta} S^{-1}_{j,i}\partial_i W(\alpha, t) \\ &+ W(\alpha, t)\left[S^{-1}\partial_{\vec{\alpha}}\left(V - \frac{1}{2\beta}\ln|S|\right)\right]^j\Bigg\},\end{aligned} \tag{24}$$

which has the equilibrium distribution $W_{eq}(\alpha)$ satisfying

$$\begin{aligned}&\sum_i \frac{1}{\beta} S^{-1}_{j,i}\partial_i W_{eq}(\alpha) + W_{eq}(\alpha) \\ &\quad \times \sum_i S^{-1}_{j,i}\partial_i\left(V - \frac{1}{2\beta}\ln|S|\right) = 0.\end{aligned} \tag{25}$$

Indeed, by multiplying both sides of the equations by $S_{k,j}$ and summing over j, we obtain the standard equation for the equilibrium distribution $\sqrt{|S|}\exp(-\beta V)$.

IV. COVARIANT LANGEVIN DYNAMICS FOR IONS AND ELECTRONS

We want to implement the above formalism in an *ab initio* molecular dynamics at finite temperature dealing with electrons and ions within the same formalism, similarly to what was done in the pioneering work by Car and Parrinello.[2] In the following, we will show how the ionic motion can be quite naturally included in the above scheme. In fact, what we obtained before does not hold only for the electronic parameters, but for a generic set of parameters which appear in a variational wave function. The ionic positions $\mathbf{R}$ can thus be thought as complementary parameters. The inclusion of this kind of parameters in the above formalism is straightforward: if M is the number of atoms, then S becomes a $(p + 3M) \times (p + 3M)$ block-diagonal matrix. The mixed elements $S_{\{\alpha\},\{\mathbf{R}\}}$ are always zero since total wave functions characterized by different sets of atomic positions are orthogonal. Moreover, since the ionic positions $\mathbf{R}$ belong to the real space, the corresponding metric is the Cartesian one, and is defined by a diagonal matrix $S(R_l, R_r) = S_N\delta_{l,r}$ among all the ion components. Thus, we can explicitly write down the complete set of equations for both the atomic and electronic parameters. For the ionic positions, we use

$$\begin{aligned}R(t_{n+1})^l &= R(t_n)^l + \Delta_N F^l(t_n, \{\alpha(t_n)\}) + \chi_n^l \\ \left\langle \chi_n^l \chi_n^r\right\rangle &= \frac{2\Delta_N}{\beta}\delta_{l,r}\end{aligned} \tag{26}$$

with $l, r = 1, \ldots, 3M$ and F^l being the force acting on the lth ionic Cartesian coordinate, while for the electronic variables Eq. (22) holds with $i, j = 1, \ldots, p$ and where $-\partial_{\vec{\alpha}} V$ is the force acting on the parameters α, i.e., the gradient of the total electronic energy V evaluated at fixed $\mathbf{R}$ with respect to these parameters.

Notice also that the time discretization corresponding to the ionic dynamics is defined by the arbitrary constant S_N appearing in the extended metric tensor defined before, namely, $\Delta_N = \Delta S_N^{-1}$. It is clear therefore that the relative speed between electron and ion dynamics can be tuned to optimize efficiency, exactly as in Car-Parrinello *ab initio* molecular dynamics. We emphasize here that in the limit $\Delta, \Delta_N \to 0$ consistent results are obtained because the equilibrium distribution (23) remains unaffected by the choice of S_N.

V. RESULTS AND DISCUSSION

Once we set up the discretized Eqs. (22) and (26), we can test the above formalism in a simple but realistic case. We are going to study the H_2 molecule, looking at the temperature behaviour of the total energy E and the bond distance r between the two hydrogen atoms, assumed classical. We start with this simple system because the above quantities can be easily computed, providing therefore useful benchmarks for our technique.

According to Appendix C, the distribution sampled by means of this covariant Langevin dynamics (CLD) represents an improvement on the gsBO only above a temperature T^*. At $T = 0$, our approximate free energy F_Q coincides with the gsBO one F_{BO}, but as soon as $T > 0$ the F_{BO} becomes better for $T \leq T^*$.

If the temperature is much lower than the electronic gap, the gsBO approximation should be essentially exact and can be easily obtained from the potential energy surface $v(r)$ of the H_2 molecule.

In the following, we are going to show that, in this simple system, we cannot distinguish the correct BO low temperature behavior and the one implied by our approximate technique,

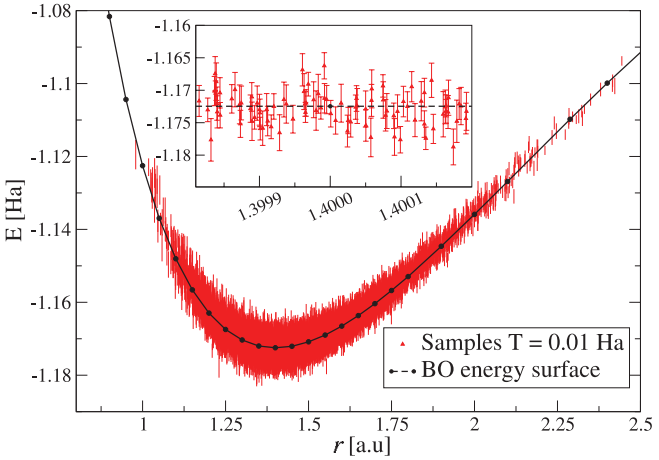

FIG. 1. (Black line) Total energy E as a function of the bond length r obtained by minimizing the energy of our variational wave function for fixed r; in doing this, we act only on those Jastrow parameters $\{\alpha\}$, for which we have been able to compute the covariant forces in Eq. (22). (Red points) Energy with error bars of configurations sampled in the dynamics (22) and (26) with $T = 0.01$ Ha. The PES is correctly followed during the simulation. In the inset, a region around the minimum at $r = 1.40$ a.u. is enlarged.

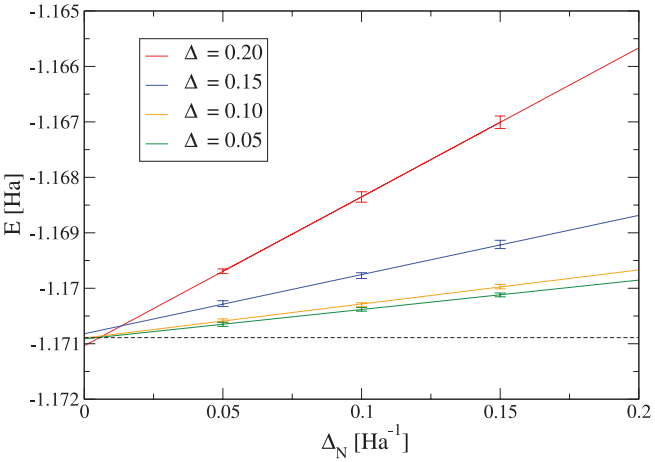

FIG. 2. Time averages of the total energy E at $T = 0.003$ Ha as a function of Δ_N for four values of Δ. All the series converge roughly to the same value, which is also the expected one (horizontal dashed line) obtained with Eq. (28). Thus, the second extrapolation $\Delta \to 0$ is not necessary.

clearly indicating that T^* should be almost negligible for this system.

To proceed further, we need now to specify what type of correlated variational wave function (4) will be used in all the following calculations, and its dependence on the two electronic positions $\vec{r}_1$ and $\vec{r}_2$. In the singlet state, the orbital function $f(\vec{r}_1, \vec{r}_2)$ is symmetric and positive and is parametrized here as a product of two factors $f(\vec{r}_1, \vec{r}_2) = f_0(\vec{r}_1, \vec{r}_2) \times \exp(J(\vec{r}_1, \vec{r}_2))$, where f_0 is taken fixed and allows to satisfy the electron-electron and electron-ion cusp conditions, whereas

$$J = \sum_{i,j} \lambda_{i,j} \phi_i(\vec{r}_1) \phi_j(\vec{r}_2) \tag{27}$$

is cusp free and is expanded systematically in a basis of atomic orbitals centered on each atom containing up to $3s$ and $1p$ gaussian functions and a constant one $\phi_0 = 1$. This amounts to $p = 65$ independent variational parameters for the symmetric matrix $\lambda_{i,j}$. The exponents of the gaussians are kept fixed during our simulations. Despite this limitation in the choice of the basis, this is acceptable for the H_2 molecule in a physically relevant range of distances between the atoms, as it is shown in Fig. 1.

The chosen variational ansatz is particularly useful for evaluating the complicated terms in (22), i.e., the *drift-diffusion* ones which depend linearly on the temperature and require the knowledge of the derivative of the matrix S. This is indeed simpler for the parameters $\lambda_{i,j}$ appearing in a linear fashion in the exponential factor J of Eq. (27). The first step is thus to construct the PES of the molecule (Fig. 1). In this way, we not only acquire the key information for the numerically exact evaluation of the gsBO observables, but we also check that our choice of the free variational parameters in the wave function allows us to recover the well known PES for this molecule.[42,43]

Canonical averages of an observable $O(r)$ can be obtained by computing numerically the one dimensional (conditionally convergent) integral

$$\hat{O} = \frac{\int dr r^2 O(r) \exp(-\beta v(r))}{\int dr r^2 \exp(-\beta v(r))}. \tag{28}$$

On the other hand, we can compute $\hat{O}$ as a time average on the Langevin dynamics (22) and (26) for sufficient low T. The extrapolation $\Delta \to 0$ involving the discretized time steps is performed in the order $\Delta_N \to 0$, $\Delta \to 0$. It is observed (see Fig. 2) that the Δ_N dependence of the time averages of the quantities is linear for fixed Δ, a property useful in the extrapolation.

Finally, we show our results for the total energy and the bond distance at various temperatures in the range between 0.001 and 0.01 Ha, i.e., from room temperature to ~3000 K. The forces acting on the parameters and on the ions, as well as the matrix S are evaluated by a short QMC run at each iteration of the dynamics. In Figs. 3 and 4, we show the outcome of our CLD simulations.

We see that our Langevin dynamics gives results in very good agreement with the expected gsBO values. We stress once again that this dynamics does not require an electronic minimization at each ionic move, realizing an impressive gain from the point of view of the computational cost. On the other hand, this kind of dynamics should behave differently with respect to the standard BOMD one when the temperature is raised and for $T > T^*$ should be more realistic, because corresponding to a more accurate upper bound of the exact free energy F. In Figures 3 and 4, we limit the study of the average energy and bond length in a range of temperatures smaller than 3000 K because, above this value, first dissociation events start to appear during the simulations. This temperature is in good qualitative agreement with low pressures experiments.[44] Roughly speaking, the dissociation probability depends on the ratio between the thermal energy T and the depth of the free energy well ΔU through the Boltzmann weight[45] $\exp(-\Delta U/T)$ within the assumption that

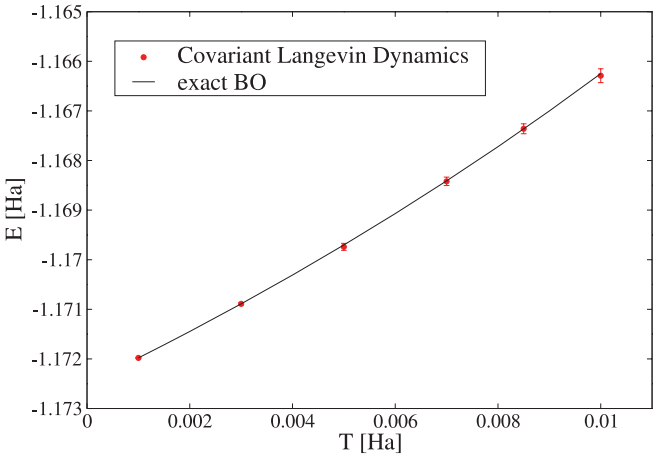

FIG. 3. Total energy E as a function of temperature. The range of temperatures is well below the electronic gap ~ 0.17 Ha (see Fig. 1) and therefore the expected exact value is the gsBO one evaluated by Eq. (28) (black line). Red points are obtained by integrating the coupled Eqs. (22) and (26). Data are in agreement with the predicted values.

excited electronic eigenstates are well-separated in energy from the ground state. There are instead examples[46] in which BO approximation breaks down, particularly near the transition state of a chemical reaction. In fact, as the reaction coordinate r increases, the energy gap between the ground state and the first (antibonding) excited state becomes smaller,[42] for example, when $r > 4$ a.u. this quantity becomes smaller than 8000 K. Therefore, large fluctuations in the bond length, certainly occurring at large temperatures, are in principle not well described under a BO scheme. Since by definition, an atomic dissociation requires to sample correctly events with large r, we expect to find differences between the standard BOMD and the dynamics generated by (22) and (26), at large enough temperatures. In Fig. 5, we observe that the probability of dissociation is enhanced in our dynamics, which can take implicitly into account also the effective repulsion due to the antibonding state. As expected, this is in sharp contrast with a DFT-BO dynamics obtained using the QUANTUM ESPRESSO package.[47,48] In the latter dynamics, large fluctuations in r do

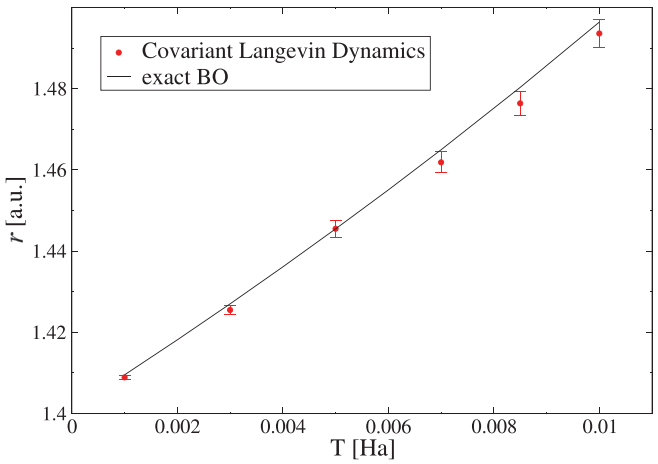

FIG. 4. Bond length r as a function of temperature. Even for this observable the Langevin dynamics (red points) give values compatible with the expected ones (black line).

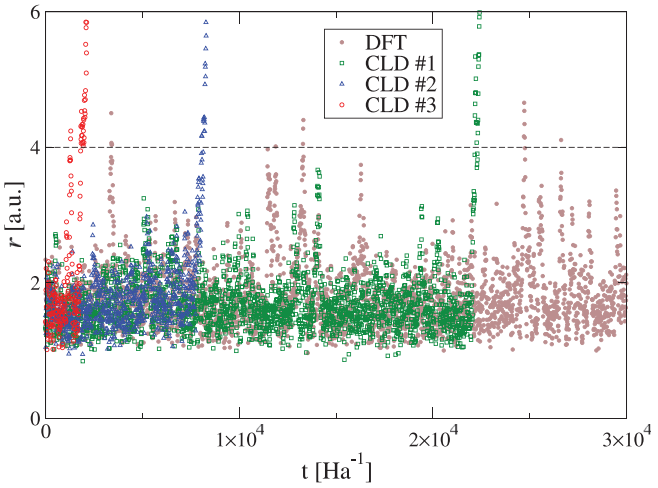

FIG. 5. Bond length r as a function of simulation time at a temperature of $T = 8000$ K. Coloured points (red, green and blue) correspond to simulations performed with the dynamics presented in this work, while the grey solid ones are obtained with a DFT-first order Langevin gsBOMD (the finite temperature BOMD, defined with the fractional occupation[4,5] yields qualitatively similar results). The time step used in the integration of the equations is $\Delta_N = 0.1$ Ha^{-1} and points are plotted every 100 iterations. The dashed line indicates the distance r^* such that the energy gap between the ground state PES and the first excited one becomes smaller than T. All the CLD trajectories show escape events while the DFT one describes a stable molecular configuration up to 20×10^4 Ha^{-1} of simulation time (not shown).

not lead to dissociation, as is partially shown in Fig. 5, and the H_2 molecule remains stable even when the finite temperature DFT is adopted with the usual practice to work with fractional occupations of the Kohn-Sham energy levels. Indeed, no escape events occur within DFT BOMD, even for long simulations. Moreover, in order to compensate the well known overbinding error[49] of the local density approximation (LDA), we have increased the temperature by a factor proportional to the LDA energy barrier ($\sim$1.40 times larger than the exact one), and observed no qualitative changes in the trajectories, always confined around the minimum energy value. It is clear therefore that, quite generally, the BOMD greatly underestimates the evaluation of the reaction rate if, for instance, a *mean first-passage time*[45] analysis is performed. However, the time scale used in this first order Langevin dynamics does not have a real physical meaning and accurate transition rates cannot be computed without extending the method to second order dynamics, by taking into account also the mass of the particles.

VI. CONCLUSIONS

In this paper, we have introduced a new promising approach to deal with finite temperature simulations of electronic systems. The approach is general and, as we have emphasized in the introduction, can be easily extended to several branches of the electronic simulations, from *ab initio* finite temperature simulations of realistic systems based on Hartree-Fock, DFT, or quantum Monte Carlo methods, to finite temperature simulations of strongly correlated Hamiltonians defined on a lattice. In particular, this technique allows us to improve systematically the gsBO approximation in a

temperature range where the quantum effects on atoms are negligible. In principle, also these quantum effects can be dealt in a simple way. To this purpose it is enough to define a quantum ansatz $|\alpha\rangle$ describing electrons and ion coordinates quantum mechanically, including in $\{\alpha\}$ also variational parameters corresponding to the atomic wave function $\Phi(\mathbf{R})$, for instance described by gaussians centered around the average atomic positions. In that case, the same derivation holds as electrons and ions can be dealt in the same footing, the metric matrix S having non trivial off diagonal elements between electronic and atomic variational parameters.

Although our first application is limited to the simple H_2 molecule with classical atomic coordinates, this extremely simple example already shows that it is possible to catch some qualitatively new features, that are not possible to describe with the conventional BO approximation. Namely, at large enough temperature the molecule can dissociate due to non adiabatic effects.

We plan to extend our method to larger and more complex realistic systems including also the quantum effects for atoms. Unfortunately, so far we have encountered a difficulty to compute in an efficient way the metric tensor S and its derivatives for a generic correlated wave function. For this reason, at present, it looks that the penalty method[38] could be a more realistic possibility for extending our technique, because the penalty method does not require the evaluation of the derivatives of the metric tensor. Apart from this technical issue there are many open problems that can be tackled with this new technique. For instance, the determination of the magnetic transition temperature is a very important challenge in material science. In principle, by applying our technique, a reasonable estimate can be easily obtained, that includes also correlation effects. In lattice models, an old standing problem is for instance the extension of the Gutzwiller variational ansatz to finite temperature calculations. Within the variational Monte Carlo, it has been established that the Hubbard model for U/t large enough should be superconducting with a d-wave order parameter. However, it is not possible to predict within the same ansatz the much more interesting superconducting temperature and how it depends on the various details of the model, such as doping and the value of the Coulomb repulsion U/t. In our formulation, what can be done at zero temperature can be readily extended to finite temperature and the evaluation of the critical temperature should be straightforward, likewise a standard (but much more accurate because including electron correlation) mean field theory at finite temperature.

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APPENDIX A: PROOF OF THE INTEGRAL FORMULA OF EQ. (11)

In this Appendix, we use known results of differential geometry in Riemann spaces[50] with tensor metric S. In order to prove Eq. (11), it is enough to consider the complete basis,

$$|i\rangle = \prod_{n=1}^{N} c^{\dagger}_{l_i(n)}|0\rangle, \tag{A1}$$

where $l_i(n)$ is an arbitrary choice of N different integers among the L possibilities, that defines the Hilbert of space of N fermions containing $D = \binom{L}{N}$ independent states. It is simple to realize that it is enough to prove that, given two arbitrary states $|i\rangle$ and $|j\rangle$, we have

$$O_{i,j} = \int d\alpha^p \sqrt{|S|}\langle i|\alpha\rangle\langle\alpha|j\rangle = C\delta_{i,j}, \tag{A2}$$

where C is an overall constant. Indeed, by assuming that the above equation holds, we can insert in Eq. (11) the completeness $I\sum_i |i\rangle\langle i|$ in both the bra and the ket of numerator in Eq. (11) and obtain

$$\begin{aligned}
&\int d\alpha^p \sqrt{|S|}\langle\alpha|\exp(-\beta H_{\mathbf{R}})|\alpha\rangle \\
&= \sum_{i,j}\langle j|\exp(-\beta H_{\mathbf{R}})|i\rangle \int d\alpha^p \sqrt{|S|}\langle\alpha|j\rangle\langle i|\alpha\rangle \\
&= C\,\mathrm{Tr}\exp(-\beta H_{\mathbf{R}}),
\end{aligned} \tag{A3}$$

which easily proves Eq. (11).

In order to establish Eq. (A2), we can consider the group of transformations $\alpha \to \alpha'$ that leaves unchanged the metric tensor S defined by

$$U|\alpha\rangle = |\alpha'\rangle, \tag{A4}$$

where U is a unitary matrix that maps any variational ansatz α to a new variational ansatz α' of the form defined in Eq. (4). To this purpose, it is enough to consider the unitary transformations defined by

$$U_l c^{\dagger}_m U^{\dagger}_l = (1 - 2\delta_{l,m})c^{\dagger}_m, \;\; U_l = \exp(i\pi c^{\dagger}_l c_l), \tag{A5}$$

$$U_P c^{\dagger}_l U^{\dagger}_P = c^{\dagger}_{p(l)}, \tag{A6}$$

where $p(l)$ is an arbitrary permutation of the L indices. All the above transformations are real and unitary and therefore conserve the distance between two arbitrary vectors, implying that the metric ds^2 remains unchanged under all these transformations, when applied to any arbitrary state of the ansatz,

$$ds^2 = S_{i,j}(\alpha)d\alpha^i d\alpha^j = S_{i,j}(\alpha')d\alpha'^i d\alpha'^j. \tag{A7}$$

In differential geometry, these transformations are called isometries, and represent the basis for the classification of symmetric Riemann spaces. In this context, they are important to prove the main statement of this Appendix. Indeed, we can consider any isometry as a change of variable in the integral and obtain that (since the integration variables are dummy variables we can use α in place of α')

$$O_{i,j} = \int d\alpha^p \sqrt{|S|}\langle i|U^{\dagger}|\alpha\rangle\langle\alpha|U|j\rangle. \tag{A8}$$

Now since the set of states is complete the matrix elements $O_{i,j}$ define univocally an operator in the given D-dimensional

Hilbert space. Therefore, by applying the relation (A8) for all isometries U_l for $l = 1, \ldots, L$, we obtain that this operator O commutes with all fermion occupation number n_l and therefore has to be diagonal, namely, $O_{i,j} = C_i \delta_{i,j}$. On the other hand, we can apply Eq. (A8) for an arbitrary unitary permutation U_P, that is able to connect any state i of the Hilbert space to any other one $|j\rangle$, namely, $U_P|i\rangle = |j\rangle$. Thus, it easily follows that

$$O_{i,i} = \int d\alpha^p \sqrt{|S|} \langle i|U_P^\dagger|\alpha\rangle\langle\alpha|U_P|i\rangle \tag{A9}$$

$$= \int d\alpha^p \sqrt{|S|} \langle j|\alpha\rangle\langle\alpha|j\rangle = O_{j,j}, \tag{A10}$$

implying that $O_{i,i} = C_i$ does not depend on i, and this concludes the proof of this Appendix.

APPENDIX B: PROOF OF THE UPPER BOUND FOR NORMALIZED STATES

The expectation value of an operator O over a normalized state α is equivalent to average $\langle\psi_i|O|\psi_i\rangle$ over the distribution $p_i = \langle\psi_i|\alpha\rangle^2$ over the eigenstates ψ_i of the operator O. In fact, it immediately follows that $0 \le p_i \le 1$ and that $\sum_i p_i = 1$. Since for any distribution p_i and convex function f, it is well known that, from Jensen's inequality, we have

$$\langle f(H)\rangle \ge f(\langle H\rangle), \tag{B1}$$

where the symbol $\langle O\rangle$ means averaging over the distribution p_i of the operator O, namely, $\langle O\rangle = \sum_i p_i \langle\psi_i|O|\psi_i\rangle$. Since the operator H is Hermitian, H and $f(H)$ are diagonalized by the same eigenvectors, and therefore the distribution p_i is the same for both operators and relation (B1) simply follows from the convexity of f. Then by using the convexity of the function $f(x) = \exp(-x/T)$, by applying the above consideration to the operator $O = f(H)$, we obtain

$$\langle\alpha|\exp(-H/T)|\alpha\rangle \ge \exp(\langle\alpha| - H/T|\alpha\rangle), \tag{B2}$$

which concludes the proof of this Appendix.

APPENDIX C: APPROXIMATE PARTITION FUNCTION Z_Q VERSUS EXACT AND BORN-OPPENHEIMER PARTITION FUNCTIONS

In this Appendix, we want to investigate the nature of the approximation of the partition function Z_Q defined in (12) and used in this work. In order to do this, we will compare the approximate partition function Z_Q with the exact Z and the approximate gsBO Z_{BO}, in the general case when we use $p < D$ variational parameters in the normalized wave function ansatz $|\alpha\rangle$. To simplify the notations, we avoid to use the dependence on the atomic positions R. We assume that the ground state energy E_0 is non degenerate and all the eigenvalues $|E_i| \le B$, namely, the spectrum is bounded and B, as well as the maximum gap $\Delta = \mathrm{Max}_i E_i - E_0$, grows at most linearly with the number N of electrons. These assumptions are commonly satisfied by physical Hamiltonians of interacting fermions.

Within these assumptions, we will see that $Z_Q(T)$ is an approximation for $Z(T)$ better than $Z_{BO}(T)$ as long as the temperature T is larger than a crossover temperature $T^* < \bar{T}$ where $\bar{T}$ remains finite for $N \to \infty$.

As mentioned, we assume to know a complete orthonormal set $\{|i\rangle\}_{i=0,\ldots,D-1}$ of eigenstates of the Hamiltonian H that operates in a D-dimensional Hilbert space. This implies that at a given temperature T the exact partition function is

$$Z(T) = \sum_{i=0}^{D-1} e^{-E_i/T}, \tag{C1}$$

whereas the gsBO partition function is

$$Z_{BO}(T) = \exp(-E_V/T), \tag{C2}$$

where $E_V = \mathrm{Min}_\alpha \langle\alpha|H|\alpha\rangle$ and the approximate partition function Z_Q is given in Eq. (12). We remind that we have already proven, using the convexity of the exponential function, that the relation

$$Z(T) \ge Z_Q(T) \tag{C3}$$

holds for every T, and obviously $Z(T) \ge Z_{BO}(T)$.

In order to identify the more accurate approximate partition function, namely, the one with the larger bound for $Z(T)$, we consider the ratio between the Z_Q and Z_{BO},

$$\zeta_Q(T) \equiv \frac{Z_Q(T)}{Z_{BO}(T)}. \tag{C4}$$

Since $Z_Q(T)$ is essentially a classical partition function over p variables, the equipartition theorem immediately implies that

$$Z_Q(T) \propto Z_{BO}(T) T^{p/2}. \tag{C5}$$

Thus, the BO approximation is better at low enough temperature, and, our low temperature free energy $F_Q = E_V - p/2T \ln T$ is expected to be a very bad approximation of the quantum free energy especially when p is very large, just because classical and quantum free energy differ substantially at very low temperatures.

The above consideration could lead to the disappointing conclusion that $\zeta_Q(T) > 1$, namely, $F_Q(T) \le E_V$, only for very high temperatures.

However, we can easily find a lower bound for $\zeta_Q(T)$ by using that the spectrum is bounded, as assumed at the beginning of this Appendix,

$$\zeta_Q(T) = D \frac{\int d\alpha^p \sqrt{|S|} \exp(-\frac{\langle\alpha|H - E_V|\alpha\rangle}{T})}{\int d\alpha^p \sqrt{|S|}} \ge D \exp(-\Delta/T). \tag{C6}$$

When the above bound is larger than one, $\zeta_Q(T)$ is certainly larger than one, implying $F_Q \le F_{BO}$. This occurs for $T \ge \bar{T}$, where $\bar{T}$ is easily determined by $\bar{T} = \Delta/\ln D$. Hence, in the thermodynamic limit there exists a finite crossover temperature T^*, as $\Delta/\ln D$ remains finite for $N \to \infty$, according to our assumptions.

APPENDIX D: SLATER DETERMINANTS AND SYMMETRIC RIEMANN SPACES

We consider the space $\mathcal{M}$ of normalized Slater determinants in a finite dimensional Hilbert space $\mathcal{H}$ where fermions

can occupy L different one particle states, denoted by conventional creation operators $c_i^\dagger$. A Slater determinant with N electrons can be formally written in second quantization notations by means of $N \times L$ real numbers ψ_j^i,

$$|\psi\rangle = \prod_{i=1}^{N} \sum_{j=1}^{L} \psi_{i,j} c_j^\dagger |0\rangle. \tag{D1}$$

However, all the variables of the matrix ψ are highly redundant because, as well known, the Slater determinant after the linear transformations $\psi \to \hat{L}\psi$ is multiplied by a constant $|\psi\rangle \to |\hat{L}\|\psi\rangle$, where $\hat{L}$ is an arbitrary $N \times N$ matrix and $|\hat{L}|$ its determinant. It is clear that, in order to define a Slater determinant with unit norm we can consider one constraint $\langle\psi|\psi\rangle = |\psi\psi^\dagger| = 1$ over the NL variables defining the $N \times L$ matrix ψ, amounting therefore to $NL - 1$ independent real variables. By the above discussion, the wave function $|\psi\rangle$ is left invariant for all matrix transformation $\psi \to \hat{L}\psi$ with $|\hat{L}| = 1$, defining $N^2 - 1$ independent variables for $\hat{L}$. Thus, it follows that $|\psi\rangle$ can be parametrized by $(NL - 1) - (N^2 - 1) = N(L - N)$ independent real variables. In a more rigourous mathematical formalism, by neglecting an immaterial overall sign ± 1 in the definition of ψ, the space $\mathcal{M}$ represents the coset space $O(L, L - N)$, where $O(L, L - N)$ is the irreducible symmetric Riemannian space $SO(L)/S(O(N) \times O(L - N))$.[50] We remind here that $O(N)$ denotes the group of generic orthogonal matrices, whereas $SO(N)$ represents the group of orthogonal matrices with determinant one. Similarly, $O(N) \times O(L - N)$ represents the group of block diagonal matrices with $N \times N$ and $L - N \times L - N$ blocks, where each block is in turn an orthogonal matrix. Also the symbol $S(O(N) \times O(L - N))$ indicates that the determinant of this block diagonal matrix (the products of the determinant of each block, equal to ± 1 as for any orthogonal matrix) has to be 1.

This space $\mathcal{M}$ is compact (all the $N(L - N)$ independent variables represent essentially angles of unit vectors in L dimensional space) and there exists a unique (up to a constant) measure $d\mu$ such that $d\bar{U}\mu = d\mu$ for all $\bar{U} \in SO(L)$ where $SO(L)$ is the group of $L \times L$ orthogonal matrices with unit determinant,[50] namely, $|\bar{U}| = 1$. An orthogonal matrix U, acts on $|\psi\rangle$ in an obvious way, namely, $\psi \to \psi U$ in Eq. (D1). The space $\mathcal{M}$ can be therefore represented by an irreducible symmetric Riemannian space. Using a matrix $U \in SO(L)$, we have essentially L orthonormal directions (e.g., the raws of the matrix), and the first N spans all possible Slater determinants in the space $\mathcal{M}$. For the previous discussion, this Slater determinant will be left unchanged (up to a sign) if we multiply the matrix U for an arbitrary element of the $S(O(N) \times O(L - N))$ unitary group, and therefore $\mathcal{M}$ is equivalent to the space $SO(L)/S(O(N) \times O(L - N))$.

As a further proof that $\mathcal{M}$ is equivalent to $SO(L)/S(O(N) \times O(L - N))$ it is also easy to verify that the dimension of this space is exactly $N(L - N)$. The dimension of an orthogonal matrix of dimension D is $D(D - 1)/2$, and therefore the dimension of the coset space $SO(L)/S(O(N) \times O(L - N))$ is $L(L - 1)/2 - (L - N)(L - N - 1)/2 - N(N - 1)/2 = N(L - N)$. ■

In order to represent the irreducible space $SO(L)/S(O(N) \times O(L - N))$ for $L \gg N$, with $N(L - N)$ variables, a possible choice is to define an unconstrained $N \times (L - N)$ matrix V and the corresponding unitary $L \times L$ matrix Q,

$$Q = \begin{pmatrix} \sqrt{I - VV^\dagger} & V \\ -V^\dagger & \sqrt{I - V^\dagger V} \end{pmatrix}, \tag{D2}$$

with the constraint that the positive definite matrix $VV^\dagger$ has all eigenvalues bounded by one, namely, $VV^\dagger \leq 1$. Thus, we explicitly see that the space is compact. As mentioned before we can identify a wave function $\psi \in M$ with the first N raws of this unitary matrix Q, up to a sign, so that the orbitals of the determinant are

$$\psi_{l,k} = Q_{l,k} \quad \text{for} \quad l = 1, 2, \cdots, N. \tag{D3}$$

A measure $d\psi$ of the coset (reducible) Riemann space $SO(L)/S(O(N) \times O(L - N))$ is said to be an invariant measure when it remains invariant under all unitary transformations $U \in U(L)$, namely, $d\psi U = d\psi$. An invariant measure represented by the matrix V is given by

$$d\psi = C d\mu(V), \tag{D4}$$

where C is an appropriate normalization constant, and $\mu(V)$ is the invariant measure in $SU(L)/S(U(N) \times U(L - N))$.[50] Although explicit formulas are known for the invariant measure, they look a bit complicated to be implemented in practice. We are confident that a very convenient expression of the invariant measure is possible in terms of the eigenvalues of $VV^\dagger$, which should amount to only N^3 operations. This would lead immediately to a computationally affordable extension of our method to DFT or mean-field type of ansatz.

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