Condensed matter from a many-electron point of view

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I. MICROSCOPIC DESCRIPTION OF CONDENSED MATTER

There is very little doubt about the microscopic physical laws underlying all condensed matter, and the following non-relativistic Hamiltonian is expected to provide a precise quantitative description for the many different phases, solid, liquid, metals, insulators, etc, observed in our daily life

$$H = T + V \tag{1}$$

$$T = T_n + T_e \tag{2}$$

$$T_n = -\frac{\hbar^2}{2m_n}\sum_I \nabla_I^2, \qquad T_e = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 \tag{3}$$

$$V(\mathbf{r},\mathbf{R}) = \sum_{i<j}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|} + \sum_{I<J}\frac{Z^2e^2}{|\mathbf{R}_I-\mathbf{R}_J|} - \sum_{i,I}\frac{Ze^2}{|\mathbf{r}_i-\mathbf{R}_J|} \tag{4}$$

where $\mathbf{r}$ and $\mathbf{R}$ denotes the set of electronic and nuclear positions, $\mathbf{r}_i$ ($\mathbf{R}_I$) labels the indiviual coordinate of electron i (nucleon I) and summations over i (I) extend over all N_e electrons (N_n nuclei). Electrons and nucleons interact via the Coulomb interactions between themselves and each other, e is the electron charge. The physical problem is then set up by the Schrödinger equation for the many-body wave function, imposing appropriate boundary conditions and symmetries due to particle statistics considering electronic and nuclear spin degrees of freedom.

We are interested in the description of a macroscopic system characterized by the electronic density $n = N_e/V$ at temperature T. Despite the simplicity of the Hamiltonian, Eq. (1), extremely rich phase diagrams will emerge and a quantitative description/prediction will be challenging. In practice, we will have to make use of further (crude) approximations, even for the most simple elements, e.g. hydrogen. The difficulty is due to the very many particles, $N \sim 10^{24}$, involved in condensed matter states.

The aims of the course is to give a brief overview over some numerical and analytical methods deviced to approach this problems. Though they will in general not provide exact solutions, apart some rare cases, they provide a starting point for approximations. Having in mind the complexity of all the various phases potentially emerging from the same Hamiltonian, Eq. (1), the success of simple models, e.g. non-interacting electron models, seems to be quite fortunuous. Numerical approaches to tackle the many-particle/electron problem can help us to bridge the gap between microscopic and model descriptions.

Still, numerical approaches/solutions will in general also involve a certain number of approximations. These approximations are in general uncontrolled, in the sense that we will not be able to improve them systematically until a given precision is reached. However, our aim should be to estimate and quantify the systematic uncertainty stemming from the various approximation, if necessary. Experimental data should not be used to validate these approximations, rather, deviations with experiment should trigger reexaminations, as well as questioning the underlying description and modelling of experimental setups and their interpretation.

In the following, we will mainly focus on systems of volume V in thermodynamic equilibrium where the expectation value of any observable A at temperature $T = 1/\beta$, is given by

$$\langle A\rangle_{TV} = \frac{1}{Z}\mathrm{Tr}\left[Ae^{-\beta H}\right] \tag{5}$$

where the $Z = \mathrm{Tr}\left[e^{-\beta H}\right] = e^{-\beta F(T,V)}$ is the partition function, the logarithm defining the free energy, $F(T,V)$.

A. Path-Integral Monte Carlo calculations

Path-Integral Monte Carlo (PIMC) methods give access to sample the elements of the (unnormalized) thermal density matrix

$$\rho(\mathbf{R}'\mathbf{r}',\mathbf{R}\mathbf{r};\beta) = \langle \mathbf{R}'\mathbf{r}'|e^{-\beta H}|\mathbf{R}\mathbf{r}\rangle \tag{6}$$

from which we can calculate static expectation values of any operator at inverse temperature $\beta = 1/k_B T$.

However, since functions of operators are in general defined via their spectral representation, a direct evaluation of Eq. (6) requires knowledge of all energy eigenfunctions. Based on the Trotter formula [25]

$$e^{-\beta H} = \lim_{M\to\infty} \left(e^{-\tau T} e^{-\tau V}\right)^M, \quad \tau = \beta/M \tag{7}$$

the path integral formulation [24] circumvents explicit diagonalizations and the density matrix can be written as

$$\rho(\mathbf{R}'\mathbf{r}', \mathbf{R}\mathbf{r}; \beta) = \lim_{M\to\infty} \sum_{\mathcal{P}} (\pm 1)^{|\mathcal{P}|} \int_{\mathbf{R}\mathbf{r}}^{\mathcal{P}(\mathbf{R}'\mathbf{r}')} D\mathbf{R}[\tau] D\mathbf{r}[\tau] \left(\frac{\sqrt{m_e m_n}}{2\pi\hbar^2\beta/M}\right)^{3M} e^{-S_M^p(\mathbf{R}[\tau]\mathbf{r}[\tau];\beta)} \tag{8}$$

with $\int D\mathbf{R}[\tau] D\mathbf{r}[\tau] = \prod_{m=1}^{M-1} \int d\mathbf{R}^m \int d\mathbf{r}^m$ and

$$S_M^p(\mathbf{R}[\tau]\mathbf{r}[\tau];\beta) = \sum_{m=0}^{M-1} \left[\frac{m_n(\mathbf{R}^{m+1}-\mathbf{R}^m)^2}{2\hbar^2(\beta/M)} + \frac{m_e(\mathbf{r}^{m+1}-\mathbf{r}^m)^2}{2\hbar^2(\beta/M)} + (\beta/M) V(\mathbf{r}^m, \mathbf{R}^m)\right] \tag{9}$$

setting $(\mathbf{R}^0, \mathbf{r}^0) = (\mathbf{R}, \mathbf{r})$ and $(\mathbf{R}^M, \mathbf{r}^M) = \mathcal{P}(\mathbf{R}', \mathbf{r}')$ and the summation extends over all possible permutations $\mathcal{P}$ for correct (anti-)symmetrization. Integrals involved in the discretized path integral as well as the summation over permutations can then be sampled by Monte Carlo methods [26, 27].

The negative sign occuring for odd permutations of fermions will strongly affect the signal to noise ratio of direct Monte Carlo evaluations [4]. Such quantum statistical effects will be important below the Fermi temperature. For an ideal gas of electrons, we have $T_F^e \simeq 581\,454\, r_s^{-2}$ Kelvin, such that $T/T_F^e \lesssim 1\%$ in the our region of interest, $T \lesssim 10^3$K. The Fermi temperature of free protons, T_F^p, is considerably lower, $T_F^p = (m_e/m_p) T_F^e \simeq T_F^e/1836$, so that inter-nuclear exchange are expected to be neglectible in many systems. However, intra-molecular exchanges for para and ortho H_2 may need to be taken into account, certainly at the lower temperatures around and below the rotational energy excitations ~ 200K.

B. Adiabatic (Born-Oppenheimer) approximation

The path-integral expression above, Eq. (8) with Eq. (9), is based on the so-called primitive approximation of the short time (or high temperature) density matrix

$$\rho(\mathbf{R}'\mathbf{r}', \mathbf{R}\mathbf{r}; \tau) \approx \langle \mathbf{R}'\mathbf{r}' | e^{-\tau T} e^{-\tau V} | \mathbf{R}\mathbf{r}\rangle \sim e^{-S_1^p(\mathbf{R}'\mathbf{r}', \mathbf{R}\mathbf{r};\tau)} \tag{10}$$

choosing τ sufficiently small, such that residual effects due to the commutator $[T, V]$ can be neglected. Different short-time approximations can be chosen which may allow us to reach the same precision within larger time steps, τ, so that less discretizations M of the path are needed for our computations [26].

From physical considerations we expect that the Born-Oppenheimer approximation should provide an excellent description in our region of interest. We therefore choose a different short time approximation, $\rho(\mathbf{R}'\mathbf{r}', \mathbf{R}\mathbf{r}; \tau) \approx \rho_{BO}(\mathbf{R}'\mathbf{r}', \mathbf{R}\mathbf{r}; \tau)$ with

$$\rho_{BO}(\mathbf{R}'\mathbf{r}', \mathbf{R}\mathbf{r}; \tau) = \langle \mathbf{R}'\mathbf{r}' | e^{-\tau T_N} e^{-\tau H_e} | \mathbf{R}\mathbf{r}\rangle = \langle \mathbf{R}'\mathbf{r}' | e^{-\tau T_N} | \mathbf{R}\mathbf{r}'\rangle \langle \mathbf{R}\mathbf{r}' | e^{-\tau(T_e+V)} | \mathbf{R}\mathbf{r}\rangle \tag{11}$$

where matrix elements of $e^{-\tau T_N}$ are independent of electronic degrees of freedom and those of $e^{-\tau(T_e+V)}$ are now diagonal in the nuclear coordinates. Denoting $\Psi_n(\mathbf{r}|\mathbf{R})$ the eigenfunctions of energy $E_n(\mathbf{R})$ of the Born-Oppenheimer Hamiltonian $H_e = T_e + V$, the dependence on $\mathbf{R}$ enters only parametrically, we get

$$\rho_{BO}(\mathbf{R}'\mathbf{r}', \mathbf{R}\mathbf{r}; \tau) \sim \left(\frac{m_n}{2\pi\hbar^2\tau}\right)^{3/2} \sum_{n'} e^{-m_n(\mathbf{R}-\mathbf{R}')^2/2\hbar^2\tau - \tau E_{n'}(\mathbf{R})} \Psi_{n'}^*(\mathbf{r}'|\mathbf{R}) \Psi_{n'}(\mathbf{r}|\mathbf{R}) \tag{12}$$

In the resulting discretized path integral, we can then integrate out the electronic degrees of freedom (setting $\mathbf{r}^M = \mathbf{r}^0$ and integrating over $\mathbf{r}^0$)

$$\begin{aligned} \rho(\mathbf{R}', \mathbf{R}; \beta) &= \lim_{M\to\infty} \sum_{\mathcal{P}} (\pm 1)^{|\mathcal{P}|} \int_{\mathbf{R}}^{\mathcal{P}(\mathbf{R}')} D\mathbf{R}[\tau] D\mathbf{r}[\tau] \prod_m \rho_{BO}(\mathbf{R}^m\mathbf{r}^m, \mathbf{R}^{m+1}\mathbf{r}^{m+1}; \tau) \\ &= \lim_{M\to\infty} \sum_{\mathcal{P}} (\pm 1)^{|\mathcal{P}|} \int_{\mathbf{R}}^{\mathcal{P}(\mathbf{R}')} D\mathbf{R}[\tau] \left(\frac{m_p}{2\pi\hbar^2\beta/M}\right)^{3M/2} \sum_{n'} e^{-S_{Mn'}^{BO}(\mathbf{R}[\tau];\beta)} \end{aligned} \tag{13}$$

with

$$S^{BO}_{Mn'}(\mathbf{R}[\tau];\beta) = \sum_{m=0}^{M-1}\left[i(\mathbf{R}^{m+1}-\mathbf{R}^m)\cdot\mathbf{A}_{n'}(\mathbf{R}^{m+1},\mathbf{R}^m) + \frac{m_n(\mathbf{R}^{m+1}-\mathbf{R}^m)^2}{2\hbar^2(\beta/M)} + (\beta/M)E_{n'}(\mathbf{R}^m)\right] \tag{14}$$

where the (real-valued) vector potential $\mathbf{A}_n$ is defined by the electronic overlap integrals

$$\int d\mathbf{r}\Psi^*_n(\mathbf{r}|\mathbf{R}')\Psi_n(\mathbf{r}|\mathbf{R}) \simeq e^{-i(\mathbf{R}'-\mathbf{R})\cdot\mathbf{A}_n(\mathbf{R}',\mathbf{R})} \tag{15}$$

for $\mathbf{R}' \to \mathbf{R}$ and we have neglected non-adiabatic transitions between different electronic states. In general, we should have kept terms of order $(\mathbf{R}'-\mathbf{R})^2 \sim \hbar^2\beta/Mm_n$ to recover the exact path-integral in the limit $M \to \infty$. Neglecting these terms which are suppressed by $1/m_n$ corresponds to the Born-Oppenheimer approximation.

In the following, we will focus on the diagonal part of density matrix, $\rho(\mathbf{R},\mathbf{R};\beta)$ which determines most of the basic thermodynamic observables. Further, we will assume sufficiently high temperatures to neglect proton exchanges, and all proton paths are closed. Then, the phase term in Eq. (14) only contributes when a Berry phase is aquired during the trajectory in imaginary time. In general, this requires exceptionally high symmetry configurations, so that this adiabatic phase is frequently dropped in the Born-Oppenheimer sampling of solids and liquids.

For $T \ll T^e_F$, we may further neglect any contributions from electronic excitations, $n > 0$, and restrict to configurations within the ground state Born-Oppenheimer surface $E_0(\mathbf{R})$. However, we still have to resolve the electronic ground state problem to obtain $E_0(\mathbf{R})$ for given nuclear positions.

1. *Electronic structure calculations (DFT)*

Calculations of Born-Oppenheimer energy surfaces for solids and liquids is the subject of electronic structure theories ranging from group theoretical considerations based on symmetry assumptions to numerical *ab-initio* calculations starting from our Hamiltonian from above, $T_e + V(\mathbf{r},\mathbf{R})$. The label *ab-initio* is used to stress that the results do not depend on any explicit ad-hoc parameter introduced in an effective Hamiltonian description. However, since we do not have any tool to exactly solve Schrödinger's equation for the Born-Oppenheimer ground state energy, results of *ab-initio* are not unique but depend on the underlying (approximate) methods used.

In practice, density-functional (DFT) calculations are the most common choice used for electronic structure calculations over the last decades. In the Kohn-Sham formulation, the ground state energy of the full interacting Hamiltonian is mapped to non-interacting electrons within a mean-field potential given by the electronic density distribution. Similar to the Hartree-Fock equations, a self-consistent solution of the resulting single particle Schrödinger equation has to be found. Efficient algorithms and programs have been developped. Although the existence of such a mean-field potential is guaranteed by the theorem of Hohenberg and Kohn, but since its explicit form is unknown, approximate functionals are used in practice.

Although DFT has been spectactular successfull in the overall description of materials, detailed results vary with the underlying approximation of the functional. The choice of the approximate functional is ad-hoc, in general triggered by comparison to experiment. In the following, we will mostly focus on different methods which may allow us to judge the quality of the results without invoking experimental input.

C. Quantum Monte Carlo calculations at zero temperature

1. *Variational principle*

Quantum Monte Carlo methods at zero temperature are based on the variational principle

$$E_0 \le E_T \equiv \frac{\langle\Psi_T|H_e|\Psi_T\rangle}{\langle\Psi_T|\Psi_T\rangle} \tag{16}$$

where Ψ_T is any trial wave function obeying the same boundary conditions as our true (Born-Oppenheimer) ground state wave function Ψ_0. Here, and in the following we suppress the parametric dependence on the nuclear coordinates.

The simplest anti-symmetric trial wave function for N electrons is a Slater determinant, $\det_n \varphi_n(\mathbf{r}_i)$, for spin-polarized electrons, whereas it reduces to a product of two determinants, one for each spin-component, for a gaz of unpolarized electrons. Optimizing the variational energy obtained by a Slater determinant with respect to the orbitals, $\varphi_n(\mathbf{r})$ gives the Hartree-Fock energy.

To go beyond the Hartree-Fock approximation, we can add explicit pair correlations [29–32] to our wave function

$$\Psi_{SJ}(\mathbf{r}) = \det_{ni} \varphi_n(\mathbf{r}_i) e^{-U(\mathbf{r})} \tag{17}$$

The frequently called Jastrow factor $U(\mathbf{r})$ is symmetric under electron exchanges, e.g. $U = \sum_{i<j} u_{ee}(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{iJ} u_{ep}(|\mathbf{r}_i - \mathbf{R}_J|)$ provides an explicit size consistent and translational invariant form containing electron-electron and electron-proton correlations. In addition to the orbitals $\varphi_n(\mathbf{r})$, the one dimensional functions $u_{ee}(r)$ and $u_{ep}(r)$ need also to be determined by minimizing the resulting energy expectation value.

Backflow wave functions introduce an explicit dependence on all electron coordinates $\mathbf{r}$ into the Slater determinant [33–35]

$$\Psi_{bf}(\mathbf{r}) = \det_{ni} \varphi_n(\mathbf{q}_i(\mathbf{r})) e^{-U(\mathbf{r})} \tag{18}$$

by the use of backflow coordinates $\mathbf{q}_i(\mathbf{r})$ which need to be symmetric with respect to electron exchange holding i fix. A simple form for liquid and solid hydrogen [36] is $\mathbf{q}_i = \mathbf{r}_i + \sum_{j\neq i}(\mathbf{r}_i - \mathbf{r}_j) b_{ee}(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_J (\mathbf{r}_i - \mathbf{R}_J) b_{ep}(|\mathbf{r}_i - \mathbf{R}_J|)$ with one dimensional functions $b_{ee}(r)$ and $b_{ep}(r)$, ultimately determined by energy minimization.

Systematic improvement for many-body correlations either explicitly [37] or implicitely via an iterative (deep) structure [38–41] are possible, as well as combined with neural network representations [42–47]. In addition to providing lower energy expectation values, better trial wave functions also lower the variance of the energy,

$$\sigma_T^2 = \frac{\langle \Psi_T | H^2 | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} - \left(\frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} \right)^2 \tag{19}$$

which vanishes in case Ψ_T coincides with an exact energy eigenstate. Calculations with different classes of trial wave functions can be used for heuristic extrapolations of E_T to zero variance, thus providing an estimate for the residual energy error of the best trial wave function [38–40].

2. Variational Monte Carlo calculations

All of the wave functions described before have in common that the evaluation for a given configuration $\mathbf{r}$ is sufficiently fast for systems ranging from around ten to thousands of electrons. However, we still have to calculate and optimize E_T. Whereas the Hartree-Fock energy can still be calculated by deterministic quadrature, the integrals involved in the calculations based on correlated wave functions, e.g. Slater-Jastrow and backflow forms, involve integrations over $3N$ dimensions

$$E_T = \frac{\int d\mathbf{r} |\Psi_T(\mathbf{r})|^2 E_L(\mathbf{r})}{\int d\mathbf{r} |\Psi_T(\mathbf{r})|^2} \tag{20}$$

where we have introduced the so-called local energy

$$E_L(\mathbf{r}) \equiv \frac{\langle \mathbf{r} | H | \Psi_T \rangle}{\langle \mathbf{r} | \Psi_T \rangle} = \frac{H\Psi_T(\mathbf{r})}{\Psi_T(\mathbf{r})} \tag{21}$$

in the position representation $\Psi_T(\mathbf{r}) \equiv \langle \mathbf{r} | \Psi_T \rangle$.

In variational Monte Carlo (VMC) calculations [48–50], standard Metropolis algorithm is used to sample the $3N$ dimensional configuration space $\mathbf{r}$ according to a weight $\sim |\Psi_T(\mathbf{r})|^2$ via Markov chains. An estimate of the trial energy is then obtained by averaging the local energy over the sampled configurations

$$E_T = \mathbb{E}_{\mathbf{r}\sim\Psi_T^2}[E_L(\mathbf{r})] \tag{22}$$

This estimate is unbiased, but affected by a stochastic error of order $\sim \sqrt{\sigma_T^2 / N_{MC}}$, controlled by the number of independent Monte Carlo samples, N_{MC}. Better wave functions, not only lower the energy expectation value, but also reduce the statistical error of the VMC calculations when reducing the variance towards an exact eigenstate (zero variance principle).

3. Stochastic optimization

The variational principle is of fundamental importance, since it allows us to compare the "quality" of different trial wave functions and select our "best" one, based on an objective criterium, without invoking comparison with experiment. Within VMC we can evaluate the energy of broad classes of wave functions, those which we can evaluate efficiently fast on our computer. Above, we have described generic forms of trial wave functions, all of them contain one or several unspecified functions. Any of these (one dimensional) functions can be expanded in a basis set providing a parametrization of the wave function.

Our trial wave function $\Psi_T(\mathbf{r}|\alpha)$ thus contains potentially a very large number of parameters α. The variational principle allows us to fix them by searching for the minimum of the energy expectation value $E_T(\alpha)$. This is almost a standard minimization problem, non-linear in α and intrinsically affected by stochastic noise, since $E_T(\alpha)$ is obtained via Monte Carlo integration.

Ignoring the problem of noise for the moment, one would expand $E_T(\alpha+\delta\alpha)$ up to second order in small changes $\delta\alpha$ of our parameters and use some iterative method based on Newton's method

$$\alpha \leftarrow \alpha - [\partial_\alpha^2 E_T(\alpha)]^{-1}\partial_\alpha E_T(\alpha) \tag{23}$$

where $\partial_\alpha E_T(\alpha)$ denotes the gradient vector and $\partial_\alpha^2 E_T(\alpha)$ the second derivative (Hessian) matrix, or some variant of it [51].

Apart that the Hessian might be quite costly to calculate for large number of parameters, the inversion is likely to be corruped by the stochastic noise. Instead of trying to reduce the noise as much as possible by using long MC runs, a simple gradient descent

$$\alpha \leftarrow \alpha - \epsilon\partial_\alpha E_T(\alpha) \tag{24}$$

with learning rate ϵ can be more efficient [52].

For a real trial wave function, the gradient vector of the trial energy writes

$$\begin{aligned}\partial_\alpha E_T(\alpha) &= 2\frac{\int d\mathbf{r}\Psi_T(\mathbf{r}|\alpha)H\partial_\alpha\Psi_T(\mathbf{r}|\alpha)}{\int d\mathbf{r}\Psi_T^2(\mathbf{r}|\alpha)} - 2\frac{\int d\mathbf{r}\Psi_T(\mathbf{r}|\alpha)H\Psi_T(\mathbf{r}|\alpha)}{\int d\mathbf{r}\Psi_T^2(\mathbf{r}|\alpha)}\frac{\int d\mathbf{r}\Psi_\theta(\mathbf{r}|\alpha)\partial_\theta\Psi_\theta(\mathbf{r}|\alpha)}{\int d\mathbf{r}\Psi_T^2(\mathbf{r}|\alpha)} \\ &= 2\mathbb{E}_{\mathbf{r}\sim\Psi_T^2}[\{E_L(\mathbf{r}|\alpha)-E_T(\alpha)\}\partial_\alpha\log\Psi_T(\mathbf{r}|\alpha)]\end{aligned} \tag{25}$$

where we have used that the Hamiltonian is hermitian to obtain an unbiased estimator in the last line. The resulting stochastic gradient descent based on the Monte Carlo estimation of $\partial_\alpha E_T$ is guaranteed to converge to the minimal energy [52], even in the case of large stochastic noise. Strategies based on stochastic gradient descent, also known as stochastic reconfiguration [53], have been successfully used for minimizing very large set of variational parameters, and have been combined with machine learning approaches more recently [54–56].

4. Projector Monte Carlo methods

Propagating a wave function in imaginary time $\Psi_t(\mathbf{r}) \sim \langle\mathbf{r}|e^{-tH}|\Psi_T\rangle$, the energy expectation value $E_t = \langle\Psi_t|H|\Psi_t\rangle/\langle\Psi_t|\Psi_t\rangle$ approaches the ground state energy of the same symmetry sector exponentially fast in t. Imaginary time projection can be performed stochastically based on the path-integral representation of the propagator $\rho_e(\mathbf{r}',\mathbf{r};t) = \langle\mathbf{r}'|e^{-tH_e}|\mathbf{r}\rangle$ along the lines discussed above. In the primitive approximation for $\rho_e(\mathbf{r}',\mathbf{r};t)$ we get the variational path-integral expression (VPIMC or PIGS for path-integral ground state techniques)

$$\Psi_t^2(\mathbf{r}) \sim \frac{\int d\mathbf{r}^0\int d\mathbf{r}^{2M}\int_{\mathbf{r}^0}^{\mathbf{r}^{2M}} D\mathbf{r}[\tau]\pi(\mathbf{r}[\tau])\delta(\mathbf{r}-\mathbf{r}^M)}{\int d\mathbf{r}^0\int d\mathbf{r}^{2M}\int_{\mathbf{r}^0}^{\mathbf{r}^{2M}} D\mathbf{r}[\tau]\pi(\mathbf{r}[\tau])} \tag{26}$$

$$\pi(\mathbf{r}[\tau]) = \Psi_T(\mathbf{r}^0)e^{-S^p_{2M}(\mathbf{r}[\tau];2t)}\Psi_T(\mathbf{r}^{2M}) \tag{27}$$

In contrast to PIMC for the diagonal density matrix, Eqs (8) and (9), where the paths are periodic in imaginary time ($\mathbf{r}^0=\mathbf{r}^M$), in VPIMC, Eq. (26), the paths are open with their ends weighted by the trial wave function, $\Psi_T(\mathbf{r}^0)$ and $\Psi_T(\mathbf{r}^{2M})$, and the ground state distribution is represented in the central slice $\mathbf{r}^M$ of the path.

The primitive approximation is rarely used in this context. As ground state projector Monte Carlo methods are build on top of an optimized trial wave function, one usually wants to make advantage using it as a guiding wave

function for importance sampling. For this we introduce a similarity transformation of our Hamiltonian in the position representation

$$\widetilde{H}_e = e^{U_T(\mathbf{r})} H_e e^{-U_T(\mathbf{r})} = T_e + \frac{\hbar^2}{m_e}\sum_i [\nabla_i U_T(\mathbf{r})]\cdot\nabla_i + E_L(\mathbf{r}) \tag{28}$$

where $\Psi_T(\mathbf{r}) = e^{-U_T(\mathbf{r})}$ is used as a guiding wave function.

The propagator corresponding to $\widetilde{H}$ can then be written as

$$\begin{aligned}
\widetilde{\rho}_T(\mathbf{r}',\mathbf{r};\tau) &= \sum_n \frac{\langle\mathbf{r}'|(-\tau\widetilde{H}_e)^n|\mathbf{r}\rangle}{n!} && (29)\\
&= \sum_n \frac{e^{U_T(\mathbf{r}')}\langle\mathbf{r}'|(-\tau H_e)^n|\mathbf{r}\rangle e^{-U_T(\mathbf{r})}}{n!} && (30)\\
&= e^{U_T(\mathbf{r}')}\rho(\mathbf{r}',\mathbf{r};\tau)e^{-U_T(\mathbf{r})} && (31)
\end{aligned}$$

which shows that $\widetilde{\rho}_T$ and ρ are also related by a similarity transformation.

Let us now apply Trotter's approximation to $\widetilde{\rho}_T$ for small τ

$$\begin{aligned}
\widetilde{\rho}_T(\mathbf{r}',\mathbf{r};\tau) &\approx \langle\mathbf{r}'|e^{-\tau T_e}e^{-i\tau\sum_j(\hbar/m_e)[\nabla_j U_T]\cdot\hat{\mathbf{p}}_j}e^{-\tau E_L}|\mathbf{r}\rangle\\
&\approx \langle\mathbf{r}'|e^{-\tau T_e}|\mathbf{r}-\tau\mathbf{f}\rangle e^{-\tau E_L(\mathbf{r})} \approx e^{-\tau E_L(\mathbf{r}')}\langle\mathbf{r}'+\tau\mathbf{f}'|e^{-\tau T_e}|\mathbf{r}\rangle\\
&\sim e^{-m_e(\mathbf{r}-\mathbf{r}'-\tau\mathbf{f}')^2/2\hbar^2\tau}e^{-\tau[E_L(\mathbf{r}')+E_L(\mathbf{r})]/2} && (32)\\
&\equiv \widetilde{\rho}_T^D(\mathbf{r}'\to\mathbf{r};\tau)e^{-\tau[E_L(\mathbf{r}')+E_L(\mathbf{r})]/2} && (33)
\end{aligned}$$

where $\mathbf{f}_i = (\hbar^2/m_e)\nabla_i \log\Psi_T(\mathbf{r})$ and we have used that $e^{-ip\delta/\hbar}|x\rangle = |x+\delta\rangle$. We have split the propagator into a drifted random walk, $\widetilde{\rho}_T^D$, and a weight according to the local energy of the configurations.

However, our approximate expression involving $\widetilde{\rho}_T^D$ violates the exact relation $\widetilde{\rho}_T(\mathbf{r}',\mathbf{r};\tau)/\widetilde{\rho}_T(\mathbf{r},\mathbf{r}';\tau) = \Psi_T^2(\mathbf{r})/\Psi_T^2(\mathbf{r}')$. It is important to restore this symmetry, e.g. using

$$\widetilde{\rho}_T^{DMC}(\mathbf{r}'\to\mathbf{r};\tau) = \widetilde{\rho}_T^D(\mathbf{r}'\to\mathbf{r};\tau)\min\left[1, \frac{\Psi_T^2(\mathbf{r})}{\Psi_T^2(\mathbf{r}')}\frac{\widetilde{\rho}_T^D(\mathbf{r}\to\mathbf{r}';\tau)}{\widetilde{\rho}_T^D(\mathbf{r}'\to\mathbf{r};\tau)}\right] \tag{34}$$

which coincides with Eq. (33) up to higher order terms in τ.

We can now replace the weight of the path, Eq. (27), involved in the projection with

$$\pi(\mathbf{r}[\tau]) \approx \psi_T^2(\mathbf{r}^0)\prod_{m=0}^{2M-1}\widetilde{\rho}_T^{DMC}(\mathbf{r}^m\to\mathbf{r}^{m+1};\tau)e^{-\tau[E_L(\mathbf{r}^m)+E_L(\mathbf{r}^{m+1})]/2} \tag{35}$$

Reptation Monte Carlo (RMC) [57] adds moves where new configurations are proposed by a global shift in imaginary time, $\mathbf{r}^{m+1}\leftarrow\mathbf{r}^m$ (and, with equal probability, $\mathbf{r}^{m-1}\leftarrow\mathbf{r}^m$), dropping the configuration $\mathbf{r}^m$ with $m>2M$ ($m<0$), and creating a new configuration for the freed place $\mathbf{r}^0$ ($\mathbf{r}^{2M}$). This proposition is then accepted or refused following Metropolis' rule according to the change of the weight $\pi(\mathbf{r}[\tau])$. The autocorrelation can be further reduced with minimal modifications implementing an algorithm similar to a directed loop algorithm [58].

PIMC and RMC methods store the (discretized) path $\mathbf{r}[\tau]$, ground state properties are directly acessible in the middle of the path, $\mathbf{r}(t/2)$, Eq. (26), in the limit $t\to\infty$, $\tau = t/2M \to 0$. Both limits must be numerically extrapolated.

Let us now regard the mixed distribution $\Psi_t(\mathbf{r})\Psi_T(\mathbf{r})$ at the external ends of the path which we write

$$\begin{aligned}
f_t(\mathbf{r}) &= \Psi_t(\mathbf{r})\Psi_0(\mathbf{r}) \sim \frac{\int d\mathbf{r}^0\int d\mathbf{r}^M\int_{\mathbf{r}^0}^{\mathbf{r}^M} D\mathbf{r}[\tau]\pi_M(\mathbf{r}[\tau])\delta(\mathbf{r}-\mathbf{r}^M)}{\int d\mathbf{r}^0\int d\mathbf{r}^M\int_{\mathbf{r}^0}^{\mathbf{r}^M} D\mathbf{r}[\tau]\pi_M(\mathbf{r}[\tau])} && (36)\\
\pi_M(\mathbf{r}[\tau]) &= \psi_T^2(\mathbf{r}^0)\prod_{m=0}^{M-1}\widetilde{\rho}_T^{DMC}(\mathbf{r}^m\to\mathbf{r}^{m+1};\tau)e^{\tau\{E_T-[E_L(\mathbf{r}^m)-E_L(\mathbf{r}^{m+1})]/2\}} && (37)
\end{aligned}$$

where we have introduced the trial energy E_T, a so-far arbitrary constant corresponding to a global weight, for later use. By noting that

$$\pi_{M+1}(\mathbf{r}[\tau]) = \pi_M(\mathbf{r}[\tau])\widetilde{\rho}_T^{DMC}(\mathbf{r}^M\to\mathbf{r}^{M+1};\tau)e^{\tau\{E_T-[E_L(\mathbf{r}^{M+1})+E_L(\mathbf{r}^M)]/2\}} \tag{38}$$

we can grow the projection time t based on

$$f_{t+\tau}(\mathbf{r}) \sim \mathbb{E}_{\mathbf{r}'\sim f_t(\mathbf{r}')}\left[\widetilde{\rho}_T^{DMC}(\mathbf{r}'\to\mathbf{r};\tau)e^{\tau\{E_T-[E_L(\mathbf{r})+E_L(\mathbf{r}')/2\}}\right] \tag{39}$$

Diffusion Monte Carlo (DMC) calculations directly sample the limiting distribution $t\to\infty$, iterating Eq. (39). Starting from an initial VMC distribution of N_w "walkers" $\mathbf{r}'\sim f_0(\mathbf{r}')\equiv\Psi_T^2(\mathbf{r}')$, the walkers are displaced by a drifted random walk according to $\widetilde{\rho}_T^{DMC}(\mathbf{r}'\to\mathbf{r};\tau)$ acquiring a weight $w(\mathbf{r},\mathbf{r}')=e^{\tau\{E_T-[E_L(\mathbf{r})+E_L(\mathbf{r}')/2\}}$. A branching process is usually added to take this weight into account by keeping on average $w(\mathbf{r},\mathbf{r}')$ copies of a propagated walker. The trial energy E_T must be chosen (and eventually adapted) to keep the population of walkers asymptotically stable. The grows process of Eq. (39) will reach a stationary non-vanishing distribution, $f_\infty(\mathbf{r})\sim\Psi_T(\mathbf{r})\Psi_0(\mathbf{r})$ for a trial energy coinciding with the true ground state energy E_0 [53, 59, 60].

Since DMC can be implemented on top of VMC with very few modifications, it is by far the most applied zero temperature projection method. However, the stationary distribution $f_\infty(\mathbf{r})$ does not correspond to the ground state density unless $\Psi_T\sim\Psi_0$.. Thus, general ground state observables are not directly accessed, apart from the energy where

$$E_0=\lim_{t\to\infty}\frac{\langle\Psi_{t/2}|H|\Psi_{t/2}\rangle}{\langle\Psi_{t/2}|\Psi_{t/2}\rangle}=\lim_{t\to\infty}\frac{\langle\Psi_T|H|\Psi_t\rangle}{\langle\Psi_T|\Psi_t\rangle}=\mathbb{E}_{\mathbf{r}\sim f_\infty}E_L(\mathbf{r}) \tag{40}$$

provides an unbiased estimator of the true ground state energy.

DMC calculations need to be extrapolated to the limit of vanishing time step, $\tau\to 0$, and an infinite large population of walkers, $N_w\to\infty$. In particular, the bias due to the finite size of the population will eventually grow strongly with system size. Depending on the quality of the trial wave function, the scalability of DMC to converge to the ground state energy of large systems may be questionable [61].

5. *Fixed-node approximation*

Quite generally, the overall ground state of any (regular) Hamiltonian, is nodeless and symmetric with respect to particle exchange. Thus, all projection Monte Carlo methods described above can be directly applied to obtain the ground state of a system containing N Bosons. This is not the case for Fermions, since the ground state wave function of a Fermi system must be antisymmetric,

$$\Psi_F(\ldots,\mathbf{r}_i,\ldots,\mathbf{r}_j)=-\Psi_F(\ldots,\mathbf{r}_j,\ldots,\mathbf{r}_i),\quad\text{for any } i,j \tag{41}$$

with nodes where $\Psi(\mathbf{r})=0$, e.g. when $\mathbf{r}_i=\mathbf{r}_j$. Thus, in general, the ground state of fermions is never the lowest eigenstate of the Hamiltonian of the system. Only in particular situations which we do not address here, e.g. for some particular Hamiltonian in one spatial dimension, it can be degenerate with the bosonic ground state.

It is possible to extend the variational principle for the energy to some excited states, $|\Psi_m\rangle$ with $E_m>E_0$, imposing orthogonality of the trial wave function to all lower eigenfunctions, $\langle\Psi_T|\Psi_n\rangle=0$ for all n with $E_n<E_m$. Since the fermionic ground state wave function is the lowest eigenfunction in the space of anti-symmetric wave functions, orthogonality to states with lower energy is guaranteed by symmetry. Since VMC based methods sample $|\Psi_T(\mathbf{r})|^2\geq 0$, they can be directly applied to Fermions by using antisymmetric trial wave functions which obey Eq. (41). All of the previously discussed trial wave functions are constructed manifestly anti-symmetric based on determinants.

In contrast to VMC, Projection Monte Carlo methods stochastically sample $\Psi_0(\mathbf{r})$ which now contains negative regions where the wave function cannot be interpreted as probability. Let us try to represent a fermionic wave function, starting with

$$\Psi_T=\Psi_T^+-\Psi_T^-,\quad \Psi_T^+\geq 0,\quad \Psi_T^-\geq 0 \tag{42}$$

$$\Psi_T^+=\frac{1}{2}\left(|\Psi_T|+\Psi_T\right),\quad \Psi_T^-=\frac{1}{2}\left(|\Psi_T|-\Psi_T\right) \tag{43}$$

and diffuse $\Psi_T^\pm\geq 0$ separately. Using $|\Psi_T|$ for importance sampling, e.g. in DMC, we obtain the mixed distribution

$$f_t^\pm(\mathbf{r})=|\Psi_T(\mathbf{r})|\Psi_t^\pm(\mathbf{r}) \tag{44}$$

However, both $\Psi_t^\pm$ do have some overlap with the bosonic ground state, Ψ_B, of energy E_B,

$$\Psi_t^\pm = \frac{1}{2}\left(c_B e^{-tE_B}\Psi_B(\mathbf{r})\pm c_F e^{-tE_F}\Psi_F(\mathbf{r})+\ldots\right) \tag{45}$$

$$c_B = \int d\mathbf{r}\Psi_B(\mathbf{r})|\Psi_T(\mathbf{r})|,\quad c_F=\int d\mathbf{r}\Psi_F(\mathbf{r})\Psi_T(\mathbf{r}) \tag{46}$$

We can now calculate the expectation value of some operator for the fermionic state as

$$\langle O\rangle = \frac{\int d\mathbf{r} s(\mathbf{r}) O(\mathbf{r})(f_t^+ - f_t^-)}{\int d\mathbf{r} s(\mathbf{r})(f_t^+ - f_t^-)} = \frac{1}{\bar{s}} \frac{\int d\mathbf{r} s(\mathbf{r}) O(\mathbf{r})(f_t^+ - f_t^-)}{\int d\mathbf{r}(f_t^+ + f_t^-)} \tag{47}$$

where $s(\mathbf{r}) \equiv \Psi_T(\mathbf{r})/|\Psi_T(\mathbf{r})| = \pm 1$ and

$$\bar{s} = \frac{\int d\mathbf{r} s(\mathbf{r})(f_t^+ - f_t^-)}{\int d\mathbf{r}(f_t^+ + f_t^-)} = \frac{c_F^2 e^{-tE_F} + \ldots}{c_B^2 e^{-tE_B} + \ldots} \tag{48}$$

Therefore, we have

$$\bar{s} \sim \exp[-Nt\Delta\mathcal{E}] \tag{49}$$

where $\Delta\mathcal{E} = (E_F - E_B)/N$ is independent of N for large systems. The mean sign $\bar{s}$ in general enters in the normalization of expectation values for physical observables. Assuming a finite gap, $\mathcal{E} > 0$, between the fermionic and bosonic ground state energy per particle, $\bar{s}$ vanishes exponentially in $Nt \gg 1$. Since $\langle s^2\rangle = 1$, the variance approaches one in this limit

$$\sigma_s^2 = \overline{s^2} - \bar{s}^2 \approx 1 \gg \bar{s}^2 \sim \exp[-2Nt\Delta\mathcal{E}] \tag{50}$$

In order to get the error bar of the sign $\sim \sqrt{\sigma_s^2/N_{MC}}$ sufficiently small to resolve the value of the average sign, we roughly need

$$N_{MC} \sim \frac{1}{\bar{s}^2} \sim \exp[2Nt\Delta\mathcal{E}] \tag{51}$$

independent samples, increasing exponentially with N and t. This is called fermion sign problem.

Can we circumvent this exponential signal to noise ratio? Importance sampling DMC is based on the overlap

$$f(\mathbf{r}) = \Psi_T(\mathbf{r})\Psi_0(\mathbf{r}) \tag{52}$$

Let us consider that we have found a trial wave function with exacly the same positive and negative regions as the fermionic ground state we are looking for, so that $f(\mathbf{r}) \geq 0$ in the full configuration space. In this case, if we impose $f(\mathbf{r}) \geq 0$ during the time evolution in DMC, we expect that DMC converges to the exact fermionic ground state. What happens? Looking at the drifted random walk created by the importance sampling, imposing $f(\mathbf{r}) \geq 0$ for all $\mathbf{r}$, we reject any move $\mathbf{r} \to \mathbf{r}'$ with $\Psi_T(\mathbf{r})\Psi_T(\mathbf{r}') < 0$. Our population of walkers can be separated into two sets, positive walkers at $\mathbf{r}^+$ which satisfy $\Psi_T(\mathbf{r}^+) \geq 0$, and negative walkers at $\mathbf{r}^-$ with $\Psi_T(\mathbf{r}^-) < 0$. Postive and negative walkers are separated by the nodal surface $\mathbf{s}$ where $\Psi_T(\mathbf{r} = \mathbf{s}) \equiv 0$, and it is enough to know the exact nodal surface. Note that the nodal surface $\mathbf{r}$ is a hypersphere in $Nd - 1$ dimensions where d is the spatial dimension. For any sufficiently regular antisymmetric trial function, applying the permutation operator to any positive configuration, we obtain a negative walker, and vice versa. It is therefore sufficient to sample only the positive space as long as we are only interested in physical observables which commute with the permutation operator.

Everything above is fine, but we still do not know the nodal surface for almost all fermion problems we are interested in, so let us search for the best approximation we can do. In the fixed-node approximation, we simple impose the nodes of a given trial wave function. Once started with positive walkers, our fixed-node DMC algorithm will converges to an eigenfunction of the Hamiltonian

$$H\Psi_{FN}(\mathbf{r}) = E_{FN}\Psi_{FN}(\mathbf{r}), \quad \text{for all } \mathbf{r} \text{ in } \mathbf{r}^+, \text{ the positive region with } \Psi_T(\mathbf{r}) \geq 0 \tag{53}$$

On the nodes $\mathbf{s}$ of Ψ_T, we also have $\Psi_{FN}(\mathbf{s}) = 0$, and we can continue the wave function to the negative regions, $\mathbf{r}^-$ using permutations $\Psi_{FN}(\mathbf{r}) = (-)^{|P|}\Psi_{FN}(P\mathbf{r})$, where the permutation P can be determined from solving $\Psi_T(\mathbf{r}) = (-)^{|P|}\Psi_T(P\mathbf{r})$ for P. As long as Ψ_T is a sufficiently regular fermionic trial wave function, we can reach all configuration space by this procedure, and the continued Ψ_{FN} is a continuous antisymmetric wave function [62].

Unfortunately, the partial derivatives of the constructed FN wavefunction with respect to $\mathbf{r}_i$ are in general not continuous at the nodal surface. The variational principle does not directly apply, since the FN wave function is outside the variational space of wave functions (continuous wave functions with continuous first derivatives). However, we can smear out our wave function at a distance ϵ close to the nodes to make them sufficiently smooth to apply the variational theorem, so that the smoothed function provides an upper bound for the energy. This smoothing will increase the absolute value of the curvature $\sim \epsilon^{-1}$ close to the node and the laplacian of the kinetic energy will produce large absolute values, $\sim \varepsilon^{-1}$. However, since the wave function vanishes as ϵ, the kinetic energy contribution of the

smoothed wave function close to the nodal region $\sim \int_\epsilon \psi\nabla^2\psi \sim \epsilon$ vanishes. Therefore, the energy of our fixed-node wave function provides a true upper bound to the fermion ground state energy, E_F, [63]

$$E_F \leq E_{FN} = \frac{\int d\mathbf{r}\Psi_{FN}(\mathbf{r})E_L(\mathbf{r})\Psi_{FN}(\mathbf{r})}{\int d\mathbf{r}\Psi_{FN}(\mathbf{r})\Psi_{FN}(\mathbf{r})} \tag{54}$$

For many-body fermion problems, the fixed-node energies are the most accurate variational values and routinely used in electronic structure DMC calculations [64].

As a generalization of the fixed-node approach, the fixed-phase approximation [65] is based on a complex trial wave function

$$\Psi_T(\mathbf{r}) = A(\mathbf{r})\exp[-i\varphi(\mathbf{r})], \quad \text{with non negative amplitude } A(\mathbf{r}) \geq 0 \text{ and real phase } \varphi(\mathbf{r}) \tag{55}$$

For any given phase, we can then minimize the energy of the trial wave function for an explicitly given phase, $\varphi(\mathbf{r})$. However, since the phase is only well defined for non-vanishing amplitude, we also have to fix the nodes of the amplitude and make the wave function single valued. An argument similar to that above shows that the fixed-phase wave function provides also an upper bound for the ground state energy in the same symmetry class as Ψ_T. Fixed-phase methods are needed for treating twisted boundary conditions, see below, and for systems with broken time-reversal invariance, e.g. including magnetic field effects.

D. Finite size effects

With the methods described above, we will be able to simulate systems containing N particles (electrons or protons), typically $N \lesssim 10^3$, and one might ask how such small systems may faithfully reproduce material properties in the bulk. To eliminate surface effects, periodic boundary conditions are in general used. Still, residual effects of the underlying finite simulation cell remain and the extrapolation to the thermodynamic limit represents one of the major sources of bias.

Heuristically, for classical particles, interacting via short-range forces, exponential convergence may be expected, once the size of the simulation exceeds the correlation length. Large systems are needed approaching phase transitions where the correlation length diverges, and care is needed to correctly describe ordered phases which are in general sensitive to boundary conditions. Methods to address finite size effects having their origin in structural formation have been developped in the context of classical molecular dynamics or Monte Carlo calculations [66, 67]. In the following we will focus on finite size effects of electronic origin.

As discussed previously, we mainly focuse on temperatures are much lower than the Fermi temperature of electrons, a typical situation in condensed matter physics and material science. In contrast to the nuclei, electrons are in a strongly degenerate quantum state where the wave character dominates and the sensitivy to boundary conditions is strongly enhanced.

To illustrate finite size effects, let us consider a non-interacting gas of electrons at density $N/L^3 \sim k_F^3 \sim r_s^{-3}$ where k_F is the Fermi wave vector corresponding to the highest occupied single particle state. From the ratio of the Fermi wave length $\lambda_F = 2\pi/k_F$ to the size of the box, $\lambda_F/L \simeq 2.03N^{-1/3}$, we already see that size effects will be far from neglegible even for large simulation cells containing thousands of electrons or more.

These size effects are rather well understood. They correspond to shell effects which are already present for an ideal gas with a Slater determinant composed of the first N plane wave orbitals of wave vectors $\mathbf{k}_i$ on a discrete grid of spacing $2\pi/L$. The corresponding kinetic energy per particle, $\mathcal{T}_N^0 = T_N^0/N = N^{-1}\sum_{i=1}^N(\hbar k_i)^2/2m_e$, extrapolates irregularly to the thermodynamic limit due to the sharp Fermi surface. Imposing twisted boundary conditions on the wave function [68], $\Psi(\dots,\mathbf{r}_i+L,\dots) = e^{i\vartheta}\Psi(\dots,\mathbf{r}_i,\dots)$, the wave vectors of the plane wave orbitals are collectively deplaced, corresponding to a shifted grid $\mathbf{k}+\vartheta$. Averaging the twist angle ϑ over N_ϑ twists on a dense grid in the Brillouin zone of the simulation cell then mimics the thermodynamic limit integration $\lim_{N_\vartheta\to\infty} N_\vartheta^{-1}\sum_\vartheta\sum_{\mathbf{k}} f(\mathbf{k}+\vartheta) = V/(2\pi)^3\int d^3q f(\mathbf{q})$ for any function f. However, in a many-body calculation with fixed number of particles, twist averaged boundary conditions (TABC) do not necessarily restore a sharp Fermi surface, since exactly N orbitals of lowest single particle energies are occupied for each twist, ϑ. To reproduce the exact single particle energy with a sharp Fermi surface, the number of particles must be allowed to vary with ϑ. This is implemented in grand-canonical twist averaging (GC-TABC) [69, 70].

Further important size effects are due to the long range Coulomb interactions. Let us write down the potential energy per particle, considering only electron-electron interactions,

$$\mathcal{V}_N \equiv V_N/N = \frac{1}{2V}\sum_{\mathbf{k}\neq 0} v_k\left[S_N(k)-1\right] \tag{56}$$

where $v_k \sim k^{-2}$ is the Fourier transform of the Coulomb potential, $S_N(k) = \langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle / N$ the static structure factor, and $\rho_{\mathbf{k}} = \sum_j e^{i\mathbf{k}\cdot\mathbf{r}_j}$ the Fourier transform of the density operator.

Since $S_N(k)$ is a local operator, we may expect fast convergence to the thermodynamic limit, $S_N(k) \simeq S_\infty(k)$, by analogy of $\int d\mathbf{r}\, \Psi_N^2(\mathbf{r})$ to the configuration integral of classical systems. Then, the dominate size error is given by the replacement of the discrete summation in reciprocal space by an integration

$$\mathcal{V}_\infty - \mathcal{V}_N = \left[\int \frac{d\mathbf{k}}{(2\pi)^3} - \frac{1}{V} \sum_{\mathbf{k}\neq 0} \right] \frac{v_k}{2} \left[S_\infty(k) - 1 \right] \tag{57}$$

Nonanalytical behavior of the integrand will dominate the quadrature error. Since v_k diverges at the origin, leading order corrections can be determined by focusing on the integration around $k \to 0$. The dominating term is actually the Madelung constant, e.g. the contribution of the interaction of one particle with all its periodic imagines,

$$v_M = - \left[\int \frac{d\mathbf{k}}{(2\pi)^3} - \frac{1}{V} \sum_{\mathbf{k}\neq 0} \right] \frac{v_k}{2} \sim \sum_{\mathbf{n}\neq 0} \frac{1}{|\mathbf{n}| L} \sim N^{-1/3} \tag{58}$$

and Ewald's method should be used for evaluation [23, 66, 67].

Since $S(k) \sim k^2$ for charged system with the prefactor fixed by sum rules, the next order term corresponds to the missing term with $k = 0$ in the summation on thre rhs of Eq. (57), $\lim_{k\to 0} v_k S(k)/V \sim N^{-1}$. Similar to the Madelung constant, this term depends only on the shape of the simulation cell. Both terms are therefore easily corrected for [69].

Seemingly innocent, the quadratic behavior of $S(k)$ around the origin is due to charge density fluctuations, the plasmons. The size correction of the potential energy $\sim N^{-1}$ corresponds to include half of the zero point enery of the long wavelength plasmons which do not fit inside the simulation cell. Kinetic energy corrections will add the missing other half of the plasmon energies [69].

For neutral quantum particles, these size corrections decay slightly faster $\sim N^{-4/3}$, since the energy of the long wave length phonon modes vanish linearly in $|\mathbf{k}|$, and one can show that $S(k) \sim k$ in this case.

Understanding size effects can be a powerful tool. Using all informations of calculations at a single system size, allows us to make reliable predictions of thermodynamic limit values. This is particularly important for calculations on hydrogen discussed later, where several calculations varying system sizes are hardly affordable.

We have outlined above, that size effects on the electronic ground state energy are intrinsically connected to non-analytical behavior of the wave function. Beyond shell effects, the behavior of the structure factor $S(k) \sim k^\alpha$ for $k \to 0$ determines the exponent of the leading order power law $\mathcal{E}_\infty - \mathcal{E}_N \sim N^{-(\alpha+1)/3}$ for the total energy per particle, $\mathcal{E}_N \equiv E/N$ in the case of Coulomb interactions. Although the exponent as well as the prefactor of $S(k)$ can be determined via general considerations, inaccuracies in the trial wave function, either due to limitations of the functional form or due to insufficient optimization, might lead to deviations which then propagate to size effects.

Of course, such predictions depend crucially on the underlying assumptions, as well as on the actual values for the asymptotics, e.g. extrapolating $\lim_{k\to 0} S(k)/k^2$ from our finite size data. Estimating the error of such procedures is a difficult task. Whenever affordable, numerical extrapolations of different system sizes provide important cross-checks.

Pure numerical extrapolation of size effects is delicate as our computations actually only guarantee upper bounds to the exact ground state energies. As the computational cost for optimization as well as for projection methods like DMC strongly increase with system size, deteriations of the energies for large system sizes as compared to those predicted based on finite size corrections, may actually indicate convergence problems in the data.

Here, we have focused on the error of the ground state energy. Similar considerations apply for other observables, in particular for the pressure. Using the virial estimator for Coulomb systems, size effects on the pressure can be obtained from the separate information on kinetic and potential energy corrections.

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