First-principles path-integral renormalization-group method for Coulombic many-body systems

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An approach for obtaining the ground state of Coulombic many-body systems is presented. This approach is based on the path-integral renormalization-group method with nonorthogonal Slater determinants, is free of the negative sign problem, and can handle higher dimensional systems with consideration of the correlation effect. Furthermore, it can be easily extended to the multicomponent quantum systems that contain more than two kinds of quantum particles. According to our results obtained with the present approach, it achieves the same accuracy as the variational Monte Carlo method with a few Slater determinants and enables us to study the entire ground state consisting of electrons and nuclei without the need to use the Born-Oppenheimer approximation.

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I. INTRODUCTION

Many numerical algorithms for first-principles simulations of correlated electron systems have been proposed and applied to various systems. However, even now, the nature of the ground state still remains a challenge because of the immaturity of numerical tools in terms of reliabilities and computational costs. Reliable methods tend to require higher computational costs [1] in general. The reliability problems of the results obtained by the density functional theory were reported [1–3], for instance.

The path-integral renormalization-group (PIRG) method [4–7] was proposed to obtain the many-body ground state of model Hamiltonians such as the Hubbard one. The PIRG method does not suffer from the sign problem [8], unlike the quantum Monte Carlo method. Furthermore, the PIRG method does not limit the dimensionality of systems, unlike the density-matrix renormalization-group method, because numerical renormalization is carried out in an imaginary-time space. In the PIRG method, the ground-state wave function is expressed by a linear combination of basis states, e.g., Slater determinants, in a truncated Hilbert space. While retaining the size of the truncated Hilbert space, the optimized basis states and the ground state are projected out numerically.

To make the PIRG method applicable to first-principles Hamiltonians, we extend the PIRG method with the real-space finite-difference (RSFD) approach, in which every physical quantity is defined only on grid points in a discretized space [9–14]. In this endeavor, the process of choosing more preferable basis states becomes the main drawback with respect to the computational cost. In particular, because many grid points tend to be required in the RSFD scheme, one-body Green's functions and the Fock matrix dominate the computational cost and prevent us from applying this method to realistic systems. We briefly review the original PIRG method in Sec. II, introduce an algorithm within the framework of the RSFD approach to overcome this problem in Sec. III, and show its applicability on some systems in Secs. V A and V B.

The Born-Oppenheimer approximation is useful and is effective when nuclei are heavy. However, for relatively light atoms, it leads to real and substantive discrepancies between experimental and first-principles results, for example, in the proton transfer and proton exchange in chemical and biological reactions and in proton-tunneling phenomena. To reproduce experimental results, we must treat nuclei the same as electrons [15–26]. We introduce a possible way within the framework of the RSFD approach to deal with this problem. We extend the PIRG method so as to be applicable to the non-Born-Oppenheimer Hamiltonian in Sec. IV and show some examples in Secs. V A and V B.

II. METHODOLOGY

Now, we briefly introduce the PIRG method to facilitate later discussion. In the PIRG method, the many-body wave function Ψ is approximated with the linear combination of fully unrestricted Slater determinants $\{\Phi^p\}$, in which one-body orbitals $\{\phi_i^p\}$ are free of orthonormality constraints, namely,

$$\Psi \approx \sum_{p=1}^{N_{sd}} \Phi^p,$$

$$\Phi^p = \|\{\phi_i^p\}\| = \|\phi_1^p, \phi_2^p, \ldots, \phi_{N_{el}}^p\|. \tag{1}$$

Here, N_{sd}, N_{el}, and $\|\{\phi_i^p\}\|$ denote the number of Slater determinants, the number of electrons, and the Slater determinant constructed from the set of one-body orbitals $\{\phi_i^p\}$, respectively. Throughout this paper, spin indices are ignored for simplicity. The hardest thing of this approach is a lack of an efficient way to obtain the ground state within this restricted region. As a possible solution to this problem, the PIRG method uses the imaginary-time propagator. If and only if the inner product of the ground state $\Psi_{\mathrm{g.s.}}$ and an arbitrary initial guess $\Psi_{\mathrm{i.g.}}$ $(\Psi_{\mathrm{g.s.}}, \Psi_{\mathrm{i.g.}})$ is not equal to zero, one can prove the relation

$$\Psi_{\mathrm{g.s.}} = \exp(-\tau\hat{H})\Psi_{\mathrm{i.g.}} = [\exp(-\delta\tau\hat{H})]^{N_{beads}}\Psi_{\mathrm{i.g.}}. \tag{2}$$

Here, $\delta\tau = \tau/N_{beads}$ and $\hat{H}$ is the many-body Hamiltonian with the Coulombic electron-electron interaction. This means that merely by operating the imaginary-time propagator on

the initial guess, we can obtain the ground state. However, because operating the imaginary-time propagator generates enormous numbers of Slater determinants, the difficulty we mentioned above is not removed but simply changed into a different form. Since the reason why the imaginary-time propagator in Eq. (2) generates enormous numbers of Slater determinants is that it contains two-body operators, this approach becomes workable if two-body operators are eliminated. As is well known, by means of the auxiliary-field technique called the Stratonovich-Hubbard transformation [27–30], the two-body operators in the imaginary-time propagator can be decomposed into one-body ones even in the case of Coulombic systems, namely,

$$\exp\left[-\frac{\delta\tau}{2}\sum_{j=1}^{N_{gp}}\sum_{k=1}^{N_{gp}}\hat{n}_j v(\boldsymbol{r}_j,\boldsymbol{r}_k)\hat{n}_k\right] = Z_A^{-1}\int\left[\prod_{k=1}^{N_{gp}}dA_k(\tau)\right]\exp\left[-\delta\tau L_A + i\delta\tau\sum_{j=1}^{N_{gp}}A_j(\tau)\hat{n}_j\right], \tag{3}$$

where $\hat{n}_j$ is the number operator of electrons at site j, N_{gp} is the number of grid points,

$$v(\boldsymbol{r},\boldsymbol{r}') = \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}, \tag{4}$$

$$L_A = \frac{\delta r^3}{8\pi}\sum_{j=1}^{N_{gp}}[\nabla A_j(\tau)]^2, \tag{5}$$

$$Z_A = \int\left[\prod_{k=1}^{N_{gp}}dA_k(\tau)\right]\exp(-\delta\tau L_A), \tag{6}$$

and δr is the grid spacing. The auxiliary-field variable $A_j(\tau)$ is a real number and nothing but the electric scalar potential in the Coulomb gauge. For details on this auxiliary field, see Appendix A and Ref. [27]. Strictly speaking, the problem still remains in the case of Coulombic systems because the integral with respect to its auxiliary-field variable $A_j(\tau)$ in the range $[-\infty,+\infty]$ is required. However, we can avoid this unpractical integration by adopting a technique called *renormalization*, which truncates less important Slater determinants. This is the basic idea lying under the PIRG method.

The outline of the PIRG method is shown below for convenience (see Refs. [4,5] for more detailed information):

(a) Choose p in the range $[1,N_{sd}]$.

(b) Calculate $\xi^p=\exp(-\frac{\delta\tau}{2}\hat{H}_1)\Phi^p$ with $\hat{H}_1$ being a one-body term in the Hamiltonian $\hat{H}$. (The explicit formula of the kinetic operator in the imaginary-time propagator within the RSFD scheme is given in Appendix A.)

(c) Calculate the total energy with ξ^p instead of Φ^p. If ξ^p gives a lower energy compared with Φ^p, replace Φ^p with ξ^p. If not, keep Φ^p.

(d) Generate $\{A_i\}$ $(i=1,2,\ldots,N_{gp})$ with the probability $Z_A^{-1}\exp(-\delta\tau L_A)$.

(e) Calculate $\zeta^p=\exp(i\delta\tau\Sigma_{j=1}^{N_{gp}}A_j\hat{n}_j)\Phi^p$.

(f) Calculate the total energy with ζ^p. If ζ^p gives a lower energy compared with Φ^p, replace Φ^p with ζ^p. If not, keep Φ^p.

(g) Repeat steps (b) and (c) if the S_2 formula of the Suzuki-Trotter exponential decomposition [31] is applied to $\exp(-\delta\tau\hat{H})$, that is, if one approximates $\exp(-\delta\tau\hat{H})$ with $\exp(-\frac{\delta\tau}{2}\hat{H}_1)\exp(-\delta\tau\hat{H}_2)\exp(-\frac{\delta\tau}{2}\hat{H}_1)$. Here, we assume that the Hamiltonian $\hat{H}$ is a sum of two parts: a one-body part $\hat{H}_1$ and a two-body part $\hat{H}_2$.

(h) Repeat steps (a)–(g) until the total energy converges.

Although we modify the original PIRG method in order to handle Coulombic and multicomponent systems, those modifications do not entirely change the outline itself. Meanwhile, the computational cost of obtaining the total energy changes greatly owing to those modifications, as we describe later, so that the overall cost also changes. Roughly speaking, the entire cost is proportional to how many times the total energy is calculated, namely, how many times steps (c) and (f) are performed, and this number of repetitions varies from system to system. Therefore, in this paper, we focus on the cost of calculating the total energy (see the latter part of Sec. III).

III. DETAILS ON IMPROVING THE SCALING BEHAVIOR

With the creation (annihilation) operator of electrons at site j, $\hat{c}_j^\dagger$ $(\hat{c}_j)$, the Hamiltonian is

$$\hat{H} = \sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}}[-t_{ij}+v_{ext}(\boldsymbol{r}_i)\delta_{ij}]\hat{c}_j^\dagger\hat{c}_i + \frac{1}{2}\sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}}v(\boldsymbol{r}_i,\boldsymbol{r}_j)\hat{c}_j^\dagger\hat{c}_i^\dagger\hat{c}_i\hat{c}_j, \tag{7}$$

where t_{ij} is a discretized $\frac{1}{2}\nabla^2$. When the central finite-difference formula is employed, for example, $t_{ij}=(\delta_{i,j-1}-2\delta_{i,j}+\delta_{i,j+1})/2\delta r^2$. The total energy under the approximation [Eq. (1)] is

$$\frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\sum_{p=1}^{N_{sd}}\sum_{q=1}^{N_{sd}}\langle\Phi^p|\hat{H}|\Phi^q\rangle}{\sum_{p=1}^{N_{sd}}\sum_{q=1}^{N_{sd}}\langle\Phi^p|\Phi^q\rangle} = \frac{\sum_{p=1}^{N_{sd}}\sum_{q=1}^{N_{sd}}D^{pq}E^{pq}}{\sum_{p=1}^{N_{sd}}\sum_{q=1}^{N_{sd}}D^{pq}}. \tag{8}$$

Here,

$$E^{pq} = (D^{pq})^{-1}\langle\Phi^p|\hat{H}|\Phi^q\rangle \tag{9}$$

and

$$D^{pq} = \langle\Phi^p|\Phi^q\rangle. \tag{10}$$

Inserting Eq. (7) into Eq. (9), one obtains

$$E^{pq} = \sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}}[-t_{ij}+v_{ext}(\boldsymbol{r}_i)\delta_{ij}](D^{pq})^{-1}\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i|\Phi^q\rangle + \frac{1}{2}\sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}}v(\boldsymbol{r}_i,\boldsymbol{r}_j)(D^{pq})^{-1}\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i^\dagger\hat{c}_i\hat{c}_j|\Phi^q\rangle. \tag{11}$$

When the many-body wave function is approximated with Slater determinants, the term $\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i^\dagger\hat{c}_i\hat{c}_j|\Phi^q\rangle$ becomes (see Ref. [32] and Appendix C)

$$\begin{aligned}(D^{pq})^{-1}&\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i^\dagger\hat{c}_i\hat{c}_j|\Phi^q\rangle\\ &= (D^{pq})^{-1}\langle\Phi^p|\hat{n}_j\hat{n}_i|\Phi^q\rangle - \delta_{ij}(D^{pq})^{-1}\langle\Phi^p|\hat{n}_i|\Phi^q\rangle\\ &= (D^{pq})^{-2}\langle\Phi^p|\hat{n}_j|\Phi^q\rangle\langle\Phi^p|\hat{n}_i|\Phi^q\rangle - (D^{pq})^{-2}\\ &\quad\times\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i|\Phi^q\rangle\langle\Phi^p|\hat{c}_i^\dagger\hat{c}_j|\Phi^q\rangle. \qquad (12)\end{aligned}$$

Equation (11) is rewritten as

$$\begin{aligned}E^{pq} &= \sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}}[-t_{ij}+v_{ext}(\boldsymbol{r}_i)\delta_{ij}](D^{pq})^{-1}\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i|\Phi^q\rangle\\ &\quad+\frac{1}{2}\sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}}v(\boldsymbol{r}_i,\boldsymbol{r}_j)(D^{pq})^{-2}\{\langle\Phi^p|\hat{n}_j|\Phi^q\rangle\langle\Phi^p|\hat{n}_i|\Phi^q\rangle\\ &\quad-\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i|\Phi^q\rangle\langle\Phi^p|\hat{c}_i^\dagger\hat{c}_j|\Phi^q\rangle\}. \qquad (13)\end{aligned}$$

Thus, calculating the total energy $\langle\Psi|\hat{H}|\Psi\rangle/\langle\Psi|\Psi\rangle$ can be reduced to calculating $\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i|\Phi^q\rangle/\langle\Phi^p|\Phi^q\rangle$. A simple way of calculating $\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i|\Phi^q\rangle$ is to use the one-body Green's function, $\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i|\Phi^q\rangle/\langle\Phi^p|\Phi^q\rangle$ [4,5,33]. Introducing a $N_{gp}\times N_{el}$ coefficient matrix $[\Phi^p]$ that corresponds to a Slater determinant Φ^p,

$$|\Phi^p\rangle = \prod_{j=1}^{N_{el}}\left(\sum_{i=1}^{N_{gp}}[\Phi^p]_{ij}\hat{c}_i^\dagger\right)|0\rangle, \qquad (14)$$

the N_{gp}-dimensional jth column vector $\phi_j^p(\boldsymbol{r}_i)$ of the coefficient matrix $[\Phi^p]$, and a $N_{el}\times N_{el}$ overlapping matrix,

$$S^{pq} = [\Phi^p]^\dagger[\Phi^q], \qquad (15)$$

one has the one-body Green's function with respect to a Slater-determinant pair $\{\Phi^p,\Phi^q\}$ as

$$\begin{aligned}G_{ji}^{pq} &= (D^{pq})^{-1}\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i|\Phi^q\rangle\\ &= \{[\Phi^q]([\Phi^p]^\dagger[\Phi^q])^{-1}[\Phi^p]^\dagger\}_{ji}\\ &= \{[\Phi^q](S^{pq})^{-1}[\Phi^p]^\dagger\}_{ji}\\ &= \sum_{k=1}^{N_{el}}\sum_{l=1}^{N_{el}}\phi_k^q(\boldsymbol{r}_j)(S^{pq})_{kl}^{-1}\phi_l^{p*}(\boldsymbol{r}_i) \qquad (16)\end{aligned}$$

and

$$D^{pq} = \det S^{pq}. \qquad (17)$$

Therefore,

$$\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i|\Phi^q\rangle = D^{pq}\sum_{k=1}^{N_{el}}\sum_{l=1}^{N_{el}}\phi_k^q(\boldsymbol{r}_j)(S^{pq})_{kl}^{-1}\phi_l^{p*}(\boldsymbol{r}_i). \qquad (18)$$

Substituting $\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i|\Phi^q\rangle$ in Eq. (13) with the right-hand side of the above equation, one obtains

$$\begin{aligned}E^{pq} &= \sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}}\sum_{k=1}^{N_{el}}\sum_{l=1}^{N_{el}}(S^{pq})_{kl}^{-1}\phi_l^{p*}(\boldsymbol{r}_i)[-t_{ij}+v_{ext}(\boldsymbol{r}_i)\delta_{ij}]\phi_k^q(\boldsymbol{r}_j)\\ &\quad+\frac{1}{2}\sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}}\sum_{k=1}^{N_{el}}\sum_{l=1}^{N_{el}}\sum_{m=1}^{N_{el}}\sum_{n=1}^{N_{el}}(S^{pq})_{kl}^{-1}(S^{pq})_{mn}^{-1}\phi_l^{p*}(\boldsymbol{r}_j)\phi_n^{p*}\\ &\quad\times(\boldsymbol{r}_i)v(\boldsymbol{r}_i,\boldsymbol{r}_j)\|\phi_k^q(\boldsymbol{r}_j),\phi_m^q(\boldsymbol{r}_i)\|. \qquad (19)\end{aligned}$$

The scaling behavior of the expression shown in Eq. (13) is $O(N_{gp}^2N_{el}^2N_{sd}^2)$ because the one-body Green's function in Eq. (16), which must be calculated and stored beforehand, requires an $O(N_{gp}^2N_{el}^2N_{sd}^2)$ cost though Eq. (13) itself scales with $O(N_{gp}^2N_{sd}^2)$. Also, the behavior of the above expression [Eq. (19)] is $O(N_{gp}^2N_{el}^4N_{sd}^2)$ at a glance. Obviously, the latter is much worse than the former. However, as is known, by using Poisson's equation, the scaling behavior of the above expression can be improved to $O(N_{gp}N_{el}^4N_{sd}^2)$ [12]. It is much better than that of the former, since the first-principles calculations based on the RSFD scheme tend to require much larger N_{gp} compared with N_{el}, though it is still worse than the former with respect to N_{el}. Furthermore, it can be improved to $O(N_{gp}N_{el}^2N_{sd}^2)$ by using a tiny trick, as described below. Thus, the above expression is surely greatly preferable compared with the former. In model calculations, this consideration is not necessarily needed and has not been discussed since N_{gp} takes much smaller values.

The trick is very simple as follows. Define

$$\chi_k^{pq*}(\boldsymbol{r}_i) = \sum_{l=1}^{N_{el}}(S^{pq})_{kl}^{-1}\phi_l^{p*}(\boldsymbol{r}_i). \qquad (20)$$

Then E^{pq} in Eq. (19) can be rewritten as

$$\begin{aligned}E^{pq} &= \sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}}\sum_{k=1}^{N_{el}}\chi_k^{pq*}(\boldsymbol{r}_i)[-t_{ij}+v_{ext}(\boldsymbol{r}_i)\delta_{ij}]\phi_k^q(\boldsymbol{r}_j)\\ &\quad+\frac{1}{2}\sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}}\sum_{k=1}^{N_{el}}\sum_{m=1}^{N_{el}}\chi_k^{pq*}(\boldsymbol{r}_j)\chi_m^{pq*}(\boldsymbol{r}_i)v(\boldsymbol{r}_i,\boldsymbol{r}_j)\\ &\quad\times\|\phi_k^q(\boldsymbol{r}_j),\phi_m^q(\boldsymbol{r}_i)\|. \qquad (21)\end{aligned}$$

Clearly, Eq. (21) shows $O(N_{gp}N_{el}^2N_{sd}^2)$ scaling behavior. The scaling behavior of the present approach is the same as that of the Hartree-Fock (HF) method when N_{sd} is considered to be fixed.

We note that the functional derivative of the total energy E^{pq} with respect to ϕ_i^{p*}, $\partial E^{pq}/\partial\phi_i^{p*}$, takes the same form as that of the HF method as the total energy does and exhibits the same scaling behavior as in the case of the HF method when N_{sd} is fixed.

IV. EXTENSION TO MULTICOMPONENT SYSTEMS

Consider the non-Born-Oppenheimer Hamiltonian

$$\hat{H}_{nBO} = \hat{H}_k + \hat{H}_{int}, \qquad (22)$$

where

$$\hat{H}_k = -\sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}}t_{ij}(\hat{c}_j^\dagger\hat{c}_i + \hat{D}_j^\dagger\hat{D}_i), \qquad (23)$$

$$\hat{H}_{int} = \hat{H}_{ee} + \hat{H}_{eN} + \hat{H}_{NN}, \tag{24}$$

$$\hat{H}_{ee} = \frac{1}{2}\sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}} \hat{c}_j^\dagger \hat{c}_i^\dagger v(\boldsymbol{r}_i,\boldsymbol{r}_j)\hat{c}_i\hat{c}_j = \frac{1}{2}\sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}} \hat{n}_j v(\boldsymbol{r}_i,\boldsymbol{r}_j)\hat{n}_i - \frac{1}{2}\sum_{i=1}^{N_{gp}} \hat{n}_i v(\boldsymbol{r}_i,\boldsymbol{r}_i), \tag{25}$$

$$\hat{H}_{eN} = -\sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}} \hat{c}_j^\dagger \hat{c}_j Z v(\boldsymbol{r}_i,\boldsymbol{r}_j)\hat{D}_i^\dagger \hat{D}_i, \tag{26}$$

and

$$\hat{H}_{NN} = \frac{1}{2}\sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}} \hat{D}_j^\dagger \hat{D}_i^\dagger Z^2 v(\boldsymbol{r}_i,\boldsymbol{r}_j)\hat{D}_i\hat{D}_j = \frac{1}{2}\sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}} \hat{N}_j Z^2 v(\boldsymbol{r}_i,\boldsymbol{r}_j)\hat{N}_i - \frac{1}{2}\sum_{i=1}^{N_{gp}} \hat{N}_i Z^2 v(\boldsymbol{r}_i,\boldsymbol{r}_i). \tag{27}$$

Here, Z, $\hat{D}_j^\dagger$, $\hat{D}_j$, and $\hat{N}_j$ represent the atomic number, the creation operator, the annihilation operator, and the number operator of nuclei at site j, respectively. This $\hat{H}_{int}$ can be simply rewritten as

$$\hat{H}_{int} = \frac{1}{2}\sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}} (\hat{n}_j - Z\hat{N}_j)v(\boldsymbol{r}_j,\boldsymbol{r}_i)(\hat{n}_i - Z\hat{N}_i) - \frac{1}{2}\sum_{i=1}^{N_{gp}} (\hat{n}_i + \hat{N}_i Z^2)v(\boldsymbol{r}_i,\boldsymbol{r}_i). \tag{28}$$

Comparing H_{int} with the conventional $\hat{H}_{ee}$, one derives the auxiliary field for this system as

$$\exp\left[-\frac{\delta\tau}{2}\sum_{i=1}^{N_{gp}}\sum_{j=1}^{N_{gp}} (\hat{n}_j - Z\hat{N}_j)v(\boldsymbol{r}_j,\boldsymbol{r}_i)(\hat{n}_i - Z\hat{N}_i)\right] = Z_A^{-1}\int\left[\prod_{k=1}^{N_{gp}} dA_k(\tau)\right] \times \exp\left[-\delta\tau L_A + i\delta\tau\sum_{j=1}^{N_{gp}} A_j(\tau)(\hat{n}_j - Z\hat{N}_j)\right]. \tag{29}$$

This has the same function form as the conventional auxiliary field shown in Eq. (3) except that all the operators $\hat{n}_j$ are replaced with $\hat{n}_j - Z\hat{N}_j$. Note that i in the right-hand side of Eq. (29) is the imaginary unit.

V. EXAMPLES

A. Accuracy

In this section, we verify the accuracy of the present PIRG method on some small systems. At most, 256 grid points along each coordinate axis and 15 Slater determinants were employed under the isolated boundary condition. A $12.8\times12.8\times12.8$ bohr region was included in the calculations, namely, a grid spacing of 0.05 bohr was used. Figures 1 and 2 show the results for a hydrogen molecule. As expected, the present approach reproduces the HF result in the case of $N_{sd}=1$, and the total energy decreases as the number of Slater determinants increases. Using 15 Slater determinants, the present approach gives an accuracy comparable to that of the variational Monte Carlo (VMC) [34]. As can be seen in Fig. 2, the error caused by the incompleteness of the basis set, that is, the poverty of the grids, is quite large compared with that caused by the insufficient number of Slater determinants. Indeed, we calculated the total energy of the hydrogen molecule using 25 Slater determinants and a grid spacing of 0.1 bohr and found that the total energy at $N_{sd}=25$ is almost equal to that at $N_{sd}=15$. Therefore, to achieve a higher accuracy with the current approach, it is effective to replace the basis set with a more suitable one or to employ techniques including the double grid technique [11,12,35]. Figure 1(b) confirms that the present method produces the correct asymptotic behavior when the nuclear separation becomes large.

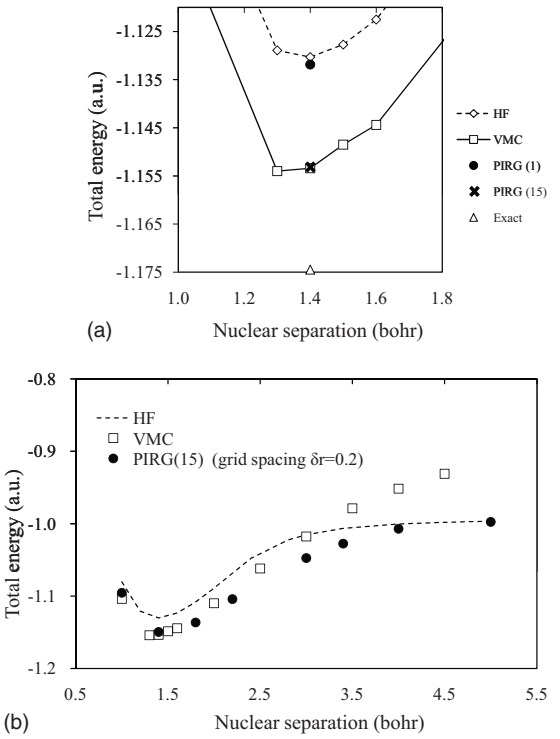

FIG. 1. (a) Total energies of hydrogen molecule obtained by various methods. The HF and VMC results are taken from Ref. [34]. The exact result is from Ref. [36]. Numbers in the parentheses after PIRG are the number of Slater determinants employed in calculations. For details on simulation conditions, see the text. (b) Total energy of a hydrogen molecule against nuclear separation. The dashed line represents results obtained by the unrestricted HF method; squares represent the VMC method [34]; and circles represent the present method using 15 Slater determinants, a grid spacing of 0.2 bohr, and the double grid technique.

"PIRG with DG" in Fig. 2 is the result obtained with a grid spacing of 0.2 bohr and the double grid technique. A noteworthy point is that the double grid technique greatly

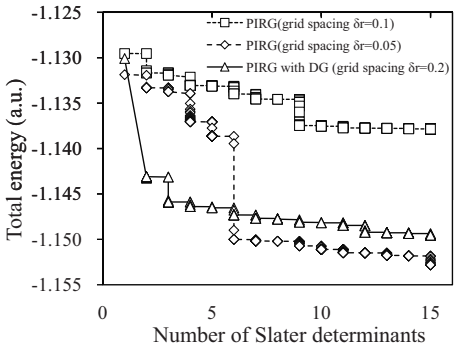

FIG. 2. Total energy of hydrogen molecule as a function of the number of Slater determinants and grid spacing. The dashed line with squares represents results obtained with a grid spacing of 0.1 bohr, the dashed line with diamonds shows results obtained with a grid spacing of 0.05 bohr, and the solid line with triangles shows results obtained with a grid spacing of 0.2 bohr and the double grid technique. Here, squares, diamonds, and triangles indicate total energies of every iteration.

improves the behavior of the present approach although the very poor basis set is employed compared with the others. Thus, PIRG with DG implies that the present approach coupled with the double grid technique and the pseudopotential technique gives a VMC-comparable accuracy with a small number of Slater determinants.

In the case of a helium atom (Fig. 3), the total energy more rapidly approaches the exact one [36], −2.903 724 52 a.u. The HF method and the VMC give −2.8617 and −2.8873 a.u., respectively [34]. Therefore, as in the case of the hydrogen molecule, the present approach reproduces the HF results when $N_{sd}=1$ and gives better results compared with the VMC when $N_{sd}\geq 6$.

B. Structural optimization

Structural optimizations and calculations of the quantum effects of nuclear motion including isotopic effects are possible applications of the extension to multicomponent systems described in Sec. V A. The significant benefits of using the PIRG method for such purposes are that it is a nonstatistical approach and that it can count the correlation effects

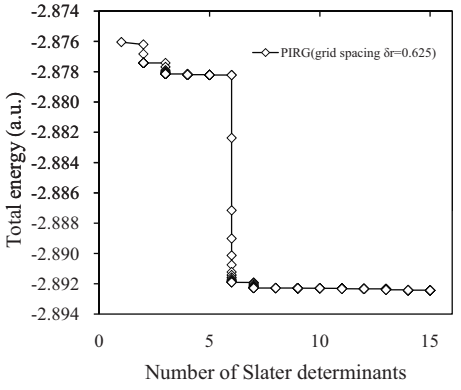

FIG. 3. Total energy of helium atom as a function of the number of Slater determinants.

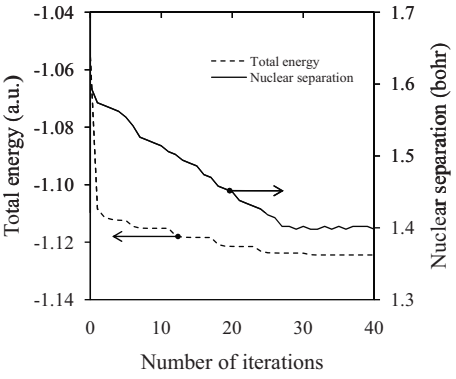

FIG. 4. Nuclear separation of hydrogen molecule as a function of number of interactions. A $12.8\times12.8\times12.8$ bohr region was taken into consideration under the isolated boundary condition. A grid spacing of 0.1 bohr and a single Slater determinant were employed.

fully in principle. Here, we demonstrate the structural optimization of small systems.

Figure 4 shows the structural optimization of the hydrogen molecule with a grid spacing of 0.1 bohr and a single Slater determinant. The two protons separated by 2.8 bohr at the beginning become closer to each other as the number of iterations increases, and finally, the nuclear separation saturates at 1.4 bohr. The imaginary-time propagators except that corresponding to the kinetic operator $-1/2\Sigma_{i=1}^{N_{gp}}\nabla^2$ change the phase of wave functions only. Namely, they leave nuclear positions untouched. Thus, nuclei were moved by the kinetic imaginary-time propagator.

As a more sophisticated example, we optimized the structures of the singlet and triplet methylenes CH_2 (see Fig. 5). We employed the double grid technique [11,12,35] and used the experimental data [37,38] to define initial structures in these calculations. The results at a grid spacing of 0.0 bohr are calculated by extrapolating data for grid spacings of 0.1 and 0.2 bohr. The calculated H-C-H angles of the singlet and triplet methylenes are 106.3° and 133.2°, respectively, and their C-H distances are 1.991 and 1.961 bohr, respectively. These results are in good agreement with the reference data [37,38].

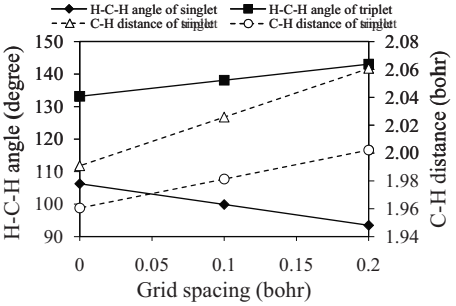

FIG. 5. H-C-H angles and C-H distances of singlet and triplet methylenes. The solid line with squares is the H-C-H angle of the singlet and that with diamonds is the H-C-H angle of the triplet. The dashed line with triangles is the C-H distance of the singlet and that with circles is the C-H distance of the triplet.

VI. CONCLUSION

We presented a method applicable to systems in which the electron-electron correlations and the quantum effects of nuclear motion are important. This method is based on the path-integral renormalization-group method with nonorthogonal Slater determinants. It is free of the negative sign problem, unlike the quantum Monte Carlo method, and does not restrict the dimensionality of systems, unlike the density-matrix renormalization-group method, with full consideration of the correlations in principle.

Our results show that the present approach can handle nuclei and correlations with only a few Slater determinants. Using 6 or 15 Slater determinants, the accuracy of the present approach becomes comparable to that of the VMC, although the error caused by the basis set is large. The result obtained with the double grid technique implies that the present approach will be a more practical and promising tool for first-principles calculations when it is combined with more accurate basis sets or the pseudopotential technique.

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APPENDIX A: AUXILIARY FIELD FOR COULOMBIC MANY-BODY SYSTEMS

We explain the derivation of the auxiliary field in Eq. (3). For an arbitrary positive-definite matrix $\boldsymbol{M}$ and positive number α, the generalized Gaussian integral formula states

$$\exp\left[-\frac{\alpha}{2}\int\int d\boldsymbol{r}d\boldsymbol{r}'\rho(\boldsymbol{r})\boldsymbol{M}(\boldsymbol{r},\boldsymbol{r}')\rho(\boldsymbol{r}')\right] = Z_A^{-1}\int\left[\prod_{\boldsymbol{r}} dA(\boldsymbol{r})\right]\exp\left[-\frac{\alpha}{2}\int\int d\boldsymbol{r}d\boldsymbol{r}'A(\boldsymbol{r}) \times\boldsymbol{M}^{-1}(\boldsymbol{r},\boldsymbol{r}')A(\boldsymbol{r}')+i\alpha\int d\boldsymbol{r}A(\boldsymbol{r})\rho(\boldsymbol{r})\right], \quad \text{(A1)}$$

where

$$Z_A=\int\left[\prod_{\boldsymbol{r}} dA(\boldsymbol{r})\right] \times\exp\left[-\frac{\alpha}{2}\int\int d\boldsymbol{r}d\boldsymbol{r}'A(\boldsymbol{r})\boldsymbol{M}^{-1}(\boldsymbol{r},\boldsymbol{r}')A(\boldsymbol{r}')\right]. \quad \text{(A2)}$$

When $\boldsymbol{M}(\boldsymbol{r},\boldsymbol{r}')=v(\boldsymbol{r},\boldsymbol{r}')$ [$=1/|\boldsymbol{r}-\boldsymbol{r}'|$ defined in Eq. (4)], $\rho(\boldsymbol{r})=\hat{n}(\boldsymbol{r})$, and $\alpha=\delta\tau$, Eq. (A1) becomes

$$\exp\left[-\frac{\delta\tau}{2}\int\int d\boldsymbol{r}d\boldsymbol{r}'\hat{n}(\boldsymbol{r})v(\boldsymbol{r},\boldsymbol{r}')\hat{n}(\boldsymbol{r}')\right] = Z_A^{-1}\int\left[\prod_{\boldsymbol{r}} dA(\boldsymbol{r})\right]\exp\left[-\frac{\delta\tau}{2}\int\int d\boldsymbol{r}d\boldsymbol{r}' \times A(\boldsymbol{r})v^{-1}(\boldsymbol{r},\boldsymbol{r}')A(\boldsymbol{r}')+i\delta\tau\int d\boldsymbol{r}A(\boldsymbol{r})\hat{n}(\boldsymbol{r})\right]. \quad \text{(A3)}$$

As is easily verified, the equation $v^{-1}(\boldsymbol{r},\boldsymbol{r}')=-\frac{1}{4\pi}\nabla^2\delta(\boldsymbol{r}-\boldsymbol{r}')$ holds since $v(\boldsymbol{r},\boldsymbol{r}')$ satisfies Poisson's equation $\nabla^2 v(\boldsymbol{r},\boldsymbol{r}')=-4\pi\delta(\boldsymbol{r}-\boldsymbol{r}')$ and

$$\begin{aligned}
&\int d\boldsymbol{r}'v(\boldsymbol{r},\boldsymbol{r}')v^{-1}(\boldsymbol{r}',\boldsymbol{r}'')\\
&=-\frac{1}{4\pi}\int d\boldsymbol{r}'\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\nabla^2\delta(\boldsymbol{r}'-\boldsymbol{r}'')\\
&=-\frac{1}{4\pi}\int d\boldsymbol{r}'\,\nabla\left[\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\nabla\,\delta(\boldsymbol{r}'-\boldsymbol{r}'')\right]\\
&\quad+\frac{1}{4\pi}\int d\boldsymbol{r}'\left(\nabla\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\right)\nabla\,\delta(\boldsymbol{r}'-\boldsymbol{r}'')\\
&=+\frac{1}{4\pi}\int d\boldsymbol{r}'\,\nabla\left[\left(\nabla\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\right)\delta(\boldsymbol{r}'-\boldsymbol{r}'')\right]\\
&\quad-\frac{1}{4\pi}\int d\boldsymbol{r}'\left(\nabla^2\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\right)\delta(\boldsymbol{r}'-\boldsymbol{r}'')\\
&=-\frac{1}{4\pi}\int d\boldsymbol{r}'[-4\pi\delta(\boldsymbol{r}-\boldsymbol{r}')]\delta(\boldsymbol{r}'-\boldsymbol{r}'')\\
&=\delta(\boldsymbol{r}-\boldsymbol{r}''). \qquad \text{(A4)}
\end{aligned}$$

The auxiliary field in Eq. (3) is finally obtained as

$$\begin{aligned}
&\exp\left[-\frac{\delta\tau}{2}\int\int d\boldsymbol{r}d\boldsymbol{r}'\hat{n}(\boldsymbol{r})v(\boldsymbol{r},\boldsymbol{r}')\hat{n}(\boldsymbol{r}')\right]\\
&=Z_A^{-1}\int\left[\prod_{\boldsymbol{r}} dA(\boldsymbol{r})\right]\exp\left[\frac{\delta\tau}{8\pi}\int d\boldsymbol{r}A(\boldsymbol{r})\nabla^2A(\boldsymbol{r})\right.\\
&\quad\left.+i\delta\tau\int d\boldsymbol{r}A(\boldsymbol{r})\hat{n}(\boldsymbol{r})\right]\\
&=Z_A^{-1}\int\left[\prod_{\boldsymbol{r}} dA(\boldsymbol{r})\right]\exp\left\{-\frac{\delta\tau}{8\pi}\int d\boldsymbol{r}[\nabla A(\boldsymbol{r})]^2\right.\\
&\quad\left.+i\delta\tau\int d\boldsymbol{r}A(\boldsymbol{r})\hat{n}(\boldsymbol{r})\right\}, \qquad \text{(A5)}
\end{aligned}$$

where

$$Z_A=\int\left[\prod_{\boldsymbol{r}} dA(\boldsymbol{r})\right]\exp\left\{-\frac{\delta\tau}{8\pi}\int d\boldsymbol{r}[\nabla A(\boldsymbol{r})]^2\right\}. \quad \text{(A6)}$$

APPENDIX B: EXACT TREATMENT OF KINETIC OPERATOR IN IMAGINARY-TIME PROPAGATOR

One possible way to treat the kinetic part in the imaginary-time propagator is to use the Taylor series about $\delta\tau=0$,

$$\exp\left[\frac{\delta\tau}{4}\nabla^2\right]=\sum_{j=0}^{k}\frac{1}{j!}\left(\frac{\delta\tau}{4}\nabla^2\right)^j+O(\delta\tau^{k+1}). \tag{B1}$$

Although the PIRG method is stable against accumulated numerical errors that originate in the above approximation, the required number of time steps to achieve a convergence may be affected. Hence, we employ the exact formula instead of Eq. (B1) within the framework of the RSFD approach. Consider discretized one-dimensional periodic systems. For these systems, the Schrödinger equation for free electrons and its solutions are given by

$$-\frac{1}{2}\frac{d^2}{dx^2}\phi_n(x_j)=\epsilon_n\phi_n(x_j), \tag{B2}$$

$$\epsilon_n=\frac{2}{\delta x^2}\sin^2\left(\frac{1}{2}G_n\delta x\right), \tag{B3}$$

$$\phi_n(x_j)=\frac{1}{\sqrt{N_{gp}}}\exp(iG_nj\delta x), \tag{B4}$$

$$G_n=\frac{2\pi n}{N_{gp}\delta x}\quad(n=1,2,\ldots,N_{gp}). \tag{B5}$$

Here, δx is the grid spacing along the x coordinate axis. The (l,m)th entry of $\exp[\frac{\delta\tau}{4}\nabla^2]$ is

$$\begin{aligned}\langle x_l|\exp\left[\frac{\delta\tau}{4}\frac{d^2}{dx^2}\right]|x_m\rangle&=\langle x_l|\exp\left[\frac{\delta\tau}{4}\frac{d^2}{dx^2}\right]\sum_{n=1}^{N_{gp}}|\phi_n\rangle\langle\phi_n|x_m\rangle\\&=\sum_{n=1}^{N_{gp}}\exp[-\delta\tau\epsilon_n/2]\langle x_l|\phi_n\rangle\langle\phi_n|x_m\rangle\\&=\frac{1}{N_{gp}}\sum_{n=1}^{N_{gp}}\exp[iG_n(l-m)\delta x-\delta\tau\epsilon_n/2].\end{aligned} \tag{B6}$$

As $|l-m|$ increases, Eq. (B6) decreases rapidly. Namely, it has a localized nature that enables us to treat it efficiently with a faster convergence, unlike Eq. (B1). It should be noted that the summation in the above equation is precomputable, and the right-hand side of the above equation becomes the modified Bessel function of the first kind with a multiplier in the limit $N_{gp}\to\infty$.

APPENDIX C: CUMULANT EXPANSION OF TWO DIFFERENT SLATER DETERMINANTS

The cumulant expansion of two-body operators sandwiched by one Slater determinant, $\langle\Phi|\hat{c}_j^\dagger\hat{c}_i^\dagger\hat{c}_i\hat{c}_j|\Phi\rangle$, is well known [32,39,40]. However, the cumulant expansion of two-body operators sandwiched by two different Slater determinants, $\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i^\dagger\hat{c}_i\hat{c}_j|\Phi^q\rangle$, is not known well, to the best of our knowledge. In this appendix, we show how such cumulant expansions are expressed in terms of one-body terms $\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i|\Phi^q\rangle$, namely, we prove Eq. (12). Note that the thing provided here is for the completion and was previously showed by Löwdin in a different way [32].

For a *biorthogonal* Slater-determinant pair $\{\xi^p,\xi^q\}$, it has been proven that two-body operators sandwiched by these Slater determinants $\langle\xi^p|\hat{c}_j^\dagger\hat{c}_i^\dagger\hat{c}_i\hat{c}_j|\xi^q\rangle$ can be expressed in terms of the one-body operators, as we previously showed (see Appendix in Ref. [41]), i.e.,

$$\langle\xi^p|\hat{c}_j^\dagger\hat{c}_i^\dagger\hat{c}_i\hat{c}_j|\xi^q\rangle=\langle\xi^p|\hat{n}_j|\xi^q\rangle\langle\xi^p|\hat{n}_i|\xi^q\rangle-\langle\xi^p|\hat{c}_j^\dagger\hat{c}_i|\xi^q\rangle\langle\xi^p|\hat{c}_i^\dagger\hat{c}_j|\xi^q\rangle. \tag{C1}$$

The word biorthogonal means that its overlap matrix $[\xi^p]^\dagger[\xi^q]$ is the identity matrix. That is, a pair $\{A,B\}$ is biorthogonal if and only if its overlap matrix $[A]^\dagger[B]$ is equal to the identity matrix.

Consider an $N_{el}\times N_{el}$ biorthogonal matrix pair $\{U^{pq},V^{pq}\}$ and an $N_{el}\times N_{el}$ regular diagonal matrix Λ^{pq}. The Slater-determinant pair $\{[\zeta^p],[\zeta^q]\}$ defined by $\{[\xi^p]U^{pq},[\xi^q]V^{pq}\}$ is biorthogonal because $[\zeta^p]^\dagger[\zeta^q]=([\xi^p]U^{pq})^\dagger[\xi^q]V^{pq}=(U^{pq})^\dagger V^{pq}=I$. The Slater determinant $[\zeta^q]\Lambda^{pq}$ is equivalent to $[\zeta^q]\times\det\Lambda^{pq}$ according to its definition [Eq. (14)]. Therefore, the cumulant expansion of the pair $\{[\Phi^p],[\Phi^q]\}$ defined by $\{[\xi^p]U^{pq},[\xi^q]\Lambda^{pq}V^{pq}\}$ is

$$\begin{aligned}&(D^{pq})^{-1}\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i^\dagger\hat{c}_i\hat{c}_j|\Phi^q\rangle\\&\quad=(D^{pq})^{-1}(\det\Lambda^{pq})\langle\zeta^p|\hat{c}_j^\dagger\hat{c}_i^\dagger\hat{c}_i\hat{c}_j|\zeta^q\rangle\\&\quad=\langle\zeta^p|\hat{c}_j^\dagger\hat{c}_i^\dagger\hat{c}_i\hat{c}_j|\zeta^q\rangle\\&\quad=\langle\zeta^p|\hat{n}_j|\zeta^q\rangle\langle\zeta^p|\hat{n}_i|\zeta^q\rangle-\langle\zeta^p|\hat{c}_j^\dagger\hat{c}_i|\zeta^q\rangle\langle\zeta^p|\hat{c}_i^\dagger\hat{c}_j|\zeta^q\rangle\\&\quad=(D^{pq})^{-2}\langle\Phi^p|\hat{n}_j|\Phi^q\rangle\langle\Phi^p|\hat{n}_i|\Phi^q\rangle-(D^{pq})^{-2}\langle\Phi^p|\hat{c}_j^\dagger\hat{c}_i|\Phi^q\rangle\\&\qquad\times\langle\Phi^p|\hat{c}_i^\dagger\hat{c}_j|\Phi^q\rangle.\end{aligned} \tag{C2}$$

Here, we used the relations $S^{pq}=[\Phi^p]^\dagger[\Phi^q]=(U^{pq})^\dagger[\xi^p]^\dagger[\xi^q]\Lambda^{pq}V^{pq}=(U^{pq})^\dagger\Lambda^{pq}V^{pq}$ and $\det\Lambda^{pq}=\det\{(U^{pq})^\dagger\Lambda^{pq}V^{pq}\}=\det S^{pq}=D^{pq}$.

Any Slater-determinant pair $\{[\Phi^p],[\Phi^q]\}$ has the corresponding biorthogonal Slater-determinant pair $\{[\xi^p],[\xi^q]\}=\{[\Phi^p](V^{pq})^\dagger,[\Phi^q](U^{pq})^\dagger(\Lambda^{pq})^{-1}\}$, where U^{pq} and V^{pq} are the biorthogonal matrices and Λ^{pq} is the regular diagonal matrix defined by $S^{pq}=(U^{pq})^\dagger\Lambda^{pq}V^{pq}$. Thus, Eq. (12) is proven.

The regularity condition of Λ^{pq} restricts the Slater-determinant pairs that this proof can handle. However, it does not emerge as a problem because for the present formulas, we assume the existence of the inverse of the overlap matrix S^{pq}.

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