Supplementary material: Random Green's function method for large-scale electronic structure calculation

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This supplementary material includes the information about the convergence of Krylov subspace and Chebyshev expansion of Fermi-Dirac operator for different materials systems including H_2O and Si clusters at different temperatures.

I. CONVERGENCE OF KRYLOV SUBSPACE WITH DIFFERENT TEMPERATURE

Based on the $v \times v$ Krylov subspace, with the overlap $O^{(i),v}_{K,mn} = \langle \Phi^{(i),v}_m | O | \Phi^{(i),v}_n \rangle$ and Hamiltonian $H^{(i),v}_{K,mn} = \langle \Phi^{(i),v}_m | H | \Phi^{(i),v}_n \rangle$, we can use the exact diagonalization method to obtain the subspace GF $\tilde{G}^{(i),v}_K(z)$ by solving the generalized eigenvalue problem,

$$H^{(i),v}_K |\Psi^{(i),v}_j\rangle = \epsilon^{(i),v}_j O^{(i),v}_K |\Psi^{(i),v}_j\rangle, \tag{1}$$

where $\epsilon^{(i),v}_j$ and $|\Psi^{(i),v}_j\rangle$ are the eigenvalues and eigenvectors with $j = 1, ..., v$. Then, we can define,

$$\tilde{G}^{(i),v}_K(z) = \sum_{j=1}^{v} \frac{|\Psi^{(i),v}_j\rangle\langle\Psi^{(i),v}_j|}{z - \epsilon^{(i),v}_j} \tag{2}$$

with which the integration within Eq.7 in the main text can be calculated analytically.
In Fig.1, we present the deviation of E_{orbit} versus the size of Krylov subspace v, to test the convergence of Krylov subspace for $(H_2O)_{526}$, $Si_{1024}H_{384}$ and $\overline{Si}_{1024}H_{384}$ clusters at different temperatures (k_BT). The chemical potential μ is set at the center of band gap (for comparing with the calculations with Chebyshev expansion).

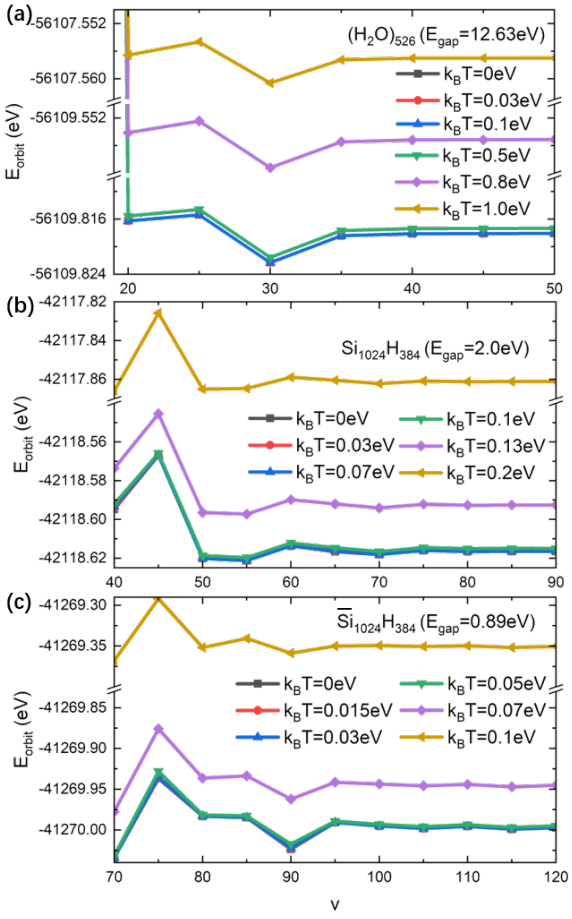

FIG. 1. Deviation of E_{orbit} versus v (the dimension of the Krylov subspace) for $(H_2O)_{526}$ (a), $Si_{1024}H_{384}$ (b), and $\overline{Si}_{1024}H_{384}$ (c) with different temperatures.

II. CONVERGENCE OF CHEBYSHEV EXPANSION WITH DIFFERENT TEMPERATURES

We have also implemented the Chebyshev expansion to compare with the Krylov projected rGF method. The Chebyshev polynomial expansion of Fermi-Dirac operator is given as[1]

$$f(H', \mu, T) = \sum_{i=0}^{N_C} c_i(\mu, T)\mathcal{T}_i(H') \tag{3}$$

where $H' = O^{-1}H$ and N_C is the total number of polynomials. $\mathcal{T}_i(H')$ is the i-th Chebyshev polynomial, which obeys the recursive relation

$$\begin{aligned} &\mathcal{T}_0(H') = 1, \quad \mathcal{T}_1(H') = H', \\ &\mathcal{T}_{i+1}(H') = 2H'\mathcal{T}_i(H') - \mathcal{T}_{i-1}(H'), \quad i \geq 1 \end{aligned} \tag{4}$$

c_i is Chebyshev expansion coefficient, which can be obtained numerically by,

$$c_i(\mu) = \int_{-1}^{1} f(\epsilon, \mu, T)\mathcal{T}_i(\epsilon)d\epsilon \tag{5}$$

Where $\epsilon = (E - \overline{E})/\Delta E$, and $\overline{E} = (E_{max} + E_{min})/2$, $\Delta E = (E_{max} - E_{min})/2$ (E_{max} and E_{min} is the maximum and minimum eigenvalue of $\hat{H}$.).
Fig.2 presents E_{orbit} versus N_C for $(H_2O)_{526}$ in (a), $Si_{1024}H_{384}$ in (b) and $\overline{Si}_{1024}H_{384}$ in (c) clusters at different temperatures(k_BT). For different systems, we can find the Chebyshev expansion and Krylov projected rGF can converge to the same results.

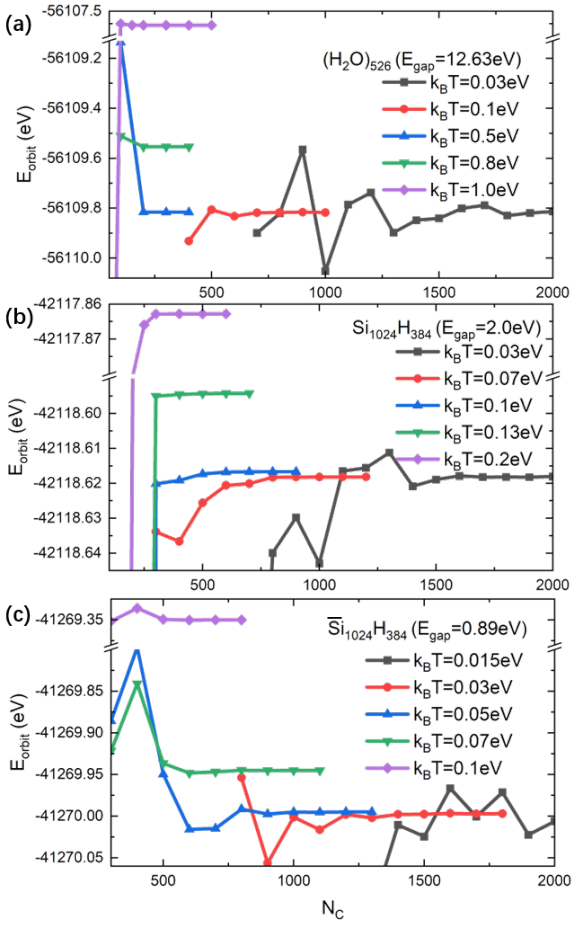

FIG. 2. Deviation of E_{orbit} versus N_C (the number of Chebyshev polynomials) for $(H_2O)_{526}$ (a), $Si_{1024}H_{384}$ (b), and $\overline{Si}_{1024}H_{384}$ (c) with different temperatures.

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[1] Y. Huang, D. J. Kouri, and D. K. Hoffmann, *Chemical Physics Letters*. 243, 367(1995)