Editors' Suggestion

Efficient Full-Frequency GW Calculations Using a Lanczos Method

Weiwei Gao,[1] Zhao Tang,[2] Jijun Zhao,[3,*] and James R. Chelikowsky[2,4,5,†]
[1]Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Ministry of Education, Dalian University of Technology, Dalian 116024, China
[2]Center for Computational Materials, Oden Institute for Computational Engineering and Sciences, The University of Texas at Austin, Austin, Texas 78712, USA
[3]Key Laboratory of Atomic and Subatomic Structure and Quantum Control (Ministry of Education), Guangdong Basic Research Center of Excellence for Structure and Fundamental Interactions of Matter, School of Physics, South China Normal University, Guangzhou 510006, China
[4]Department of Physics, The University of Texas at Austin, Austin, Texas 78712, USA
[5]McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712, USA

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The GW approximation is widely used for reliable and accurate modeling of single-particle excitations. It also serves as a starting point for many theoretical methods, such as its use in the Bethe-Salpeter equation (BSE) and dynamical mean-field theory. However, full-frequency GW calculations for large systems with hundreds of atoms remain computationally challenging, even after years of efforts to reduce the prefactor and improve scaling. We propose a method that reformulates the correlation part of the GW self-energy as a resolvent of a Hermitian matrix, which can be efficiently and accurately computed using the standard Lanczos method. This method enables full-frequency GW calculations of material systems with a few hundred atoms on a single computing workstation. We further demonstrate the efficiency of the method by calculating the defect-state energies of silicon quantum dots with diameters up to 4 nm and nearly 2,000 silicon atoms using only 20 computational nodes.

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As a first-principles approach based on many-body perturbation theory, the GW approximation has been successfully applied to accurately compute quasiparticle excitation in weakly and moderately correlated materials [1–3]. The approximation also plays an essential role in the first-principles calculations of excitonic effects using the GW + BSE approach [4,5] and is used in conjunction with other methods [6–11]. The computational scaling of different implementations of the GW approximation ranges from $O(N)$ to $O(N^6)$ and typically has a much larger prefactor compared to density functional theory (DFT) calculations with semilocal exchange-correlation functionals [12,13].

During the last decade, different formulations and algorithms have been proposed and implemented for accelerating GW calculations to meet the challenge of modeling large and complex materials [12,13]. A few seminal papers have demonstrated GW calculations of quasiparticle energies of large systems with the number of atoms ranging from 1,000 to around 2,700 [14–18]. These large-scale GW calculations rely on well-crafted numerical optimization and large computation resources. Even with notable advancements, GW calculations for systems with a few hundred atoms, which are typically required for computationally studying a point defect in solids or small quantum dots, are not performed commonly. Owing to the significant expense of data curation, GW calculations are rarely used in wide-reaching data-driven research, such as constructing large databases of material properties and training supervised machine-learning models.

In GW calculations, one of the most computationally expensive steps is calculating the frequency-dependent screened Coulomb potential W. In many implementations, the irreducible polarizability function and then the inverse dielectric function are calculated to compute W [19,20]. Such a procedure deals with the frequency dependence of W using approximations like plasmon-pole models or numerical tools such as contour deformation or analytical continuations [12,21]. Alternatively, another approach computes the reducible polarizability and W by solving the Casida equation derived in linear-response time-dependent density functional theory (TDDFT)[22–26]. Once all the eigenvalues and eigenvectors of the Casida equation are solved, the frequency-dependent W and GW quasiparticle self-energies can be written and computed in a closed form [23–25]. While this approach is formally simple and works efficiently for small systems with less than 40 atoms, it becomes numerically intractable for large systems due to the high cost of solving the Casida equation.

Here, we propose a method that avoids solving the Casida equation while still allowing us to perform full-frequency GW calculations analytically and efficiently.

To better illustrate the concept, we discuss our method applied to finite systems, for which real-valued wave functions and simplified notations can be used. We perform DFT calculations to obtain Kohn-Sham orbitals $|\phi_m\rangle$ and their corresponding energies ϵ_m, which are used as an initial approximation for quasiparticle wave functions and energies, respectively. Next, the Casida equation can be constructed [22–24,26,27]:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} X^s \\ Y^s \end{pmatrix} = \begin{pmatrix} X^s \\ Y^s \end{pmatrix} \Omega_s. \tag{1}$$

The dimension of matrices $\mathbf{A}$ and $\mathbf{B}$ is N_{vc}^2, where $N_{vc} = N_v \cdot N_c$ scales as $O(N^2)$ with respect to system size N. Here N_v and N_c represent the number of occupied and empty orbitals, respectively. With the random-phase approximation (RPA) used in the GW approximation, the matrix elements of $\mathbf{A}$ and $\mathbf{B}$ are given as

$$\mathbf{A}_{vc,v'c'} = (\epsilon_c - \epsilon_v)\delta_{vv'}\delta_{cc'} + (vc|v'c') \tag{2}$$

$$\begin{aligned} \mathbf{B}_{vc,v'c'} &= (vc|c'v') \\ &= \int\int \frac{\phi_v(\mathbf{r})\phi_c(\mathbf{r})\phi_{c'}(\mathbf{r}')\phi_{v'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'. \end{aligned} \tag{3}$$

We use indices v and v' for occupied states, c and c' for empty states, and k, l, n, and m for general orbitals, respectively. For finite systems, the Casida equation can be reformulated as a smaller eigenvalue problem [23,24],

$$\mathbf{C}Z^s = Z^s\Omega_s^2, \tag{4}$$

where $\mathbf{C} = (\mathbf{A}-\mathbf{B})^{1/2}(\mathbf{A}+\mathbf{B})(\mathbf{A}-\mathbf{B})^{1/2}$ is a symmetric matrix of dimension N_{vc}^2. After solving Eq. (4) for the eigenpairs (Z^s, Ω_s^2) of $\mathbf{C}$, one can compute the full-frequency GW self-energy

$$\langle\phi_m|\Sigma^{\mathrm{GW}}(\omega)|\phi_m\rangle = \Sigma_{mm}^{\mathrm{ex}} + \Sigma_{mm}^{\mathrm{corr}}(\omega), \tag{5}$$

$$\Sigma_{mm}^{\mathrm{ex}} = -\sum_v (vm|mv), \tag{6}$$

$$\Sigma_{mm}^{\mathrm{corr}}(\omega) = \sum_n^{N_v+N_c}\sum_s^{N_{vc}} \frac{W_{nm}^s W_{nm}^s}{\omega - \epsilon_n + \eta_n(\Omega_s - i\delta)} \tag{7}$$

where η_n is 1 for occupied orbitals and -1 for empty orbitals, and δ is a positive infinitesimal number to avoid singularity. The matrix elements W_{nm}^s are

$$W_{nm}^s = \sum_{vc}(nm|vc)\sqrt{\frac{\epsilon_c - \epsilon_v}{\Omega_s}} Z_{vc}^s. \tag{8}$$

The exchange part of the self-energy $\Sigma_{mm}^{\mathrm{ex}}$ is independent of frequency and relatively easy to compute, while the correlation part $\Sigma_{mm}^{\mathrm{corr}}(\omega)$ includes the frequency-dependent screening effects of dielectric responses. The poles of frequency-dependent screened effects can be determined by the eigenvalues of $\mathbf{C}$. As a result, the most expensive step of the aforementioned method is diagonalizing the Casida equation, as the computational cost scales as $O(N^6)$. To make further progress, we intend to avoid this costly step by defining a vector $|P_{nm}\rangle$ of dimension N_{vc}, which has elements given by $(P_{nm})_{vc} = (nm|vc)(\epsilon_c - \epsilon_v)^{1/2}$. Then W_{nm}^s becomes

$$W_{nm}^s = \langle P_{nm}|Z^s\rangle\Omega_s^{-\frac{1}{2}}. \tag{9}$$

$\Sigma_{mm}^{\mathrm{corr}}$ can be rewritten as

$$\Sigma_{mm}^{\mathrm{corr}}(\omega) = \sum_{n=1}^{N_v+N_c} \Sigma_{mm}^{\mathrm{corr}}(\omega, n), \tag{10}$$

where

$$\begin{aligned} \Sigma_{mm}^{\mathrm{corr}}(\omega, n) = &\frac{1}{z_n}\sum_{s=1}^{N_{vc}} \langle P_{nm}|Z^s\rangle\langle Z^s|P_{nm}\rangle \\ &\times \left[\frac{1}{\Omega_s} - \frac{1}{\Omega_s + \eta_n z_n}\right], \end{aligned} \tag{11}$$

where $z_n = \omega - \epsilon_n - i\eta_n\delta$.

Examining Eq. (11), we note the formula for $\Sigma_{mm}^{\mathrm{corr}}(\omega, n)$ is similar to a general resolvent matrix element of the form $\sum_k \langle\star|k\rangle\langle k|\star\rangle/(z-\lambda_k) = \langle\star|1/(z-\mathbf{H})|\star\rangle$, where $\mathbf{H}$ is a general Hermitian matrix with eigenvalues λ_k and eigenvectors $|k\rangle$, z is a complex number, and $|\star\rangle$ is a ket. Motivated by this observation, we reformulate Eq. (11) as the resolvent of a symmetric matrix $\mathbf{D}$

$$\Sigma_{mm}^{\mathrm{corr}}(\omega, n) = \frac{1}{z_n}\langle P_{nm}|\frac{1}{\mathbf{D}} - \frac{1}{\mathbf{D} + \eta_n z_n}|P_{nm}\rangle. \tag{12}$$

Matrix $\mathbf{D}$ satisfies $\mathbf{D}^2 = \mathbf{C}$ and its eigenvalues are the square root of those of matrix C, i.e., $\mathbf{D}Z^s = Z^s\Omega_s$. We use a gth degree polynomial function p_g to fit the square root function $p_g(x) = \sum_{k=0}^g a_k x^k \approx \sqrt{x}$ within $x \in [\min\Omega_s^2, \max\Omega_s^2]$, which is the range between minimum and maximum eigenvalues of matrix $\mathbf{C}$. Accordingly, $\mathbf{D}$ can be approximated by $\mathbf{D} = p_g(\mathbf{C}) + \Delta_g \approx p_g(\mathbf{C}) = a_0\mathbf{I} + \sum_{k=1}^g a_k\mathbf{C}^k$, where $\mathbf{I}$ is an identity matrix and the fitting error Δ_g can be controlled via the degree g of the polynomial function and fitting procedures. More discussions on Eq. (10) to Eq. (12) are presented in Sec. 1 of the Supplemental Material [28].

Given Eq. (12) and matrix $\mathbf{D}$, the Lanczos method can then be applied to efficiently compute the resolvent of matrix $\mathbf{D}$, which is an important step in calculating $\Sigma_{mm}^{\mathrm{corr}}(\omega, n)$. In the calculation of $\Sigma_{mm}^{\mathrm{corr}}(\omega)$, we prepare $|P_{nm}\rangle$ for each state n in the summation of Eq. (10), where

$|P_{nm}\rangle$ is used as the starting vector for the Lanczos tridiagonalization procedure of the symmetric matrix $\mathbf{D}$. With L steps of Lanczos iterations, one can construct a tridiagonal matrix $\mathbf{D}_L$ with dimension L in the following form:

$$\mathbf{D}_L = \begin{pmatrix} a_0 & b_1 & 0 & \ldots & 0 & 0 \\ b_1 & a_1 & b_2 & \ldots & 0 & 0 \\ 0 & b_2 & a_2 & \ldots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \ldots & a_{L-1} & b_L \\ 0 & 0 & 0 & \ldots & b_L & a_L \end{pmatrix}. \quad (13)$$

Once the tridiagonal matrix $\mathbf{D}_L$ is obtained, a resolvent matrix element [such as Eq. (12)] can be computed using the continuous fraction

$$\langle P_{nm}| \frac{1}{z-\mathbf{D}} |P_{nm}\rangle = \cfrac{1}{z - a_0 - \cfrac{b_1^2}{z - a_1 - \cfrac{b_2^2}{a_2 - \ldots}}}, \quad (14)$$

which is also known as the Haydock method [29]. The computation of Eq. (14) is efficient, and one can easily calculate the quasiparticle energies for a series of frequencies by varying z in Eq. (14). When applied to eigenvalue problems, the Lanczos algorithm can lead to ghost eigenvalues. However, applying the Lanczos method to calculate a resolvent is free of such a numerical problem [30].

There are several advantages to use the Lanczos method for computing $\Sigma^{\mathrm{corr}}_{mm}$. Solving the eigenvalue problem of the Casida matrix $\mathbf{C}$ is avoided, and the resulting full-frequency GW calculations become more efficient than the conventional method represented by Eq. (7), which explicitly requires the eigenpairs of $\mathbf{C}$. Frequency grids, analytical continuation, and approximations like plasmon-pole models are not required, as the frequency dependence of W and $\Sigma^{\mathrm{corr}}_{mm}$ are implicitly treated via Lanczos iterations. Moreover, the method is in principle applicable to any basis sets of wave functions, as our derivation does not rely on any features of specific basis functions.

As a general-purpose algorithm, Lanczos-based methods have been used in computational material science, such as computing Green's function [29], optical absorption spectra with linear-response TDDFT [31–35], and the Bethe-Salpeter equation [36]. Earlier work [37–39] applied Lanczos methods for solving the Sternheimer equation to obtain the frequency-dependent screened Coulomb potential. Recently, several new methods [40–44] have been explored to achieve efficient full-frequency GW calculations. For example, Scott *et al.* [41] adopted a block Lanczos algorithm to solve an effective Hamiltonian whose eigenvalues systematically approximate the excitation energies of GW theory. Bintrim and Berkelbach [40,45] proposed a method that does not require integration over the frequency grids. Instead, the GW quasiparticle energies are obtained by solving the eigenvalues of an effective Hamiltonian, which follows the algebraic diagrammatic construction [46]. Compared to these methods, our method does not solve the Sternheimer equation or obtain GW quasiparticle energies from the eigenvalues of an effective Hamiltonian. Instead, the frequency-dependent screened Coulomb potential is found using linear-response TDDFT within the Casida formalism, and the GW quasiparticle energies are computed from a summation of resolvent elements given by Eq. (12).

We checked the accuracy of the Lanczos-based method for the *GW* approximation by calculating the highest occupied and lowest unoccupied molecule orbital (HOMO and LUMO) energies of the GW100 set [47–50], which include 100 small close-shell molecules for benchmarking different implementations of the GW approximation. G_0W_0-level calculations are carried out throughout this work. As studied in previous work, G_0W_0-level calculations depend on the starting point, while quasiparticle self-consistent GW (QSGW) and fully self-consistent GW can alleviate the dependence of calculation results on the starting points [51–54]. Our new Lanczos method is compatible with QSGW [55] because the accelerated steps (i.e., bypassing the diagonalization of the Casida equation and using the Lanczos method to compute the correlation part of the self-energy) do not interfere with the self-consistent iterations. The Lanczos method only requires the updated quasiparticle energies and wave functions of the current iteration to start the next iteration of GW calculation. A real-space-based pseudopotential DFT code PARSEC is used in our implementation to efficiently obtain Kohn-Sham orbitals for large finite systems [56,57]. More details of our computations are presented in Sec. 2 of the Supplemental Material [28,58,59]. Figure 1(a) shows the results computed with the Lanczos method and the reference method agree well for all GW100 molecules. The mean average difference (MAD) between the results calculated using the reference method, which finds the eigenpairs of the Casida equation explicitly, and the Lanczos method is within 20 meV. Our tests also show the Lanczos-based formalism converges fast to the degree g of polynomial p_g and the number of Lanczos iterations N_{iter}. As shown in Figs. 1(b) and 1(c), the MAD is below 30 meV when the polynomial degree $g \geq 8$ and $N_{\mathrm{iter}} \geq 5$.

The computationally expensive steps in our method are: (1) calculating electron-repulsion integrals $(kl|nm)$ and (2) calculating the matrix-vector product $\mathbf{D}|\star\rangle$, where $|\star\rangle$ is a general vector. One can use suitable low-rank approximation methods, such as resolution-of-identity or density-fitting methods [60–62], to speed up these computations. Density-fitting methods exploit the rank deficiency of

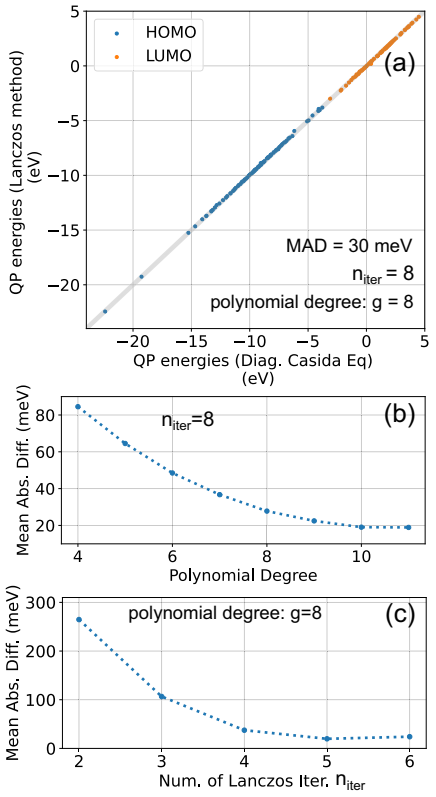

FIG. 1. (a) Comparison between the HOMO and LUMO energies calculated with the reference method and the Lanczos method. (b) The mean absolute differences (MADs) between the quasiparticle energies of one hundred small molecules calculated with the reference approach and the Lanczos method with different degrees of polynomial functions. (c) MAD of quasiparticle energies calculated with the reference method and the Lanczos method using different numbers of iterations N_{iter}.

orbital pair products $\phi_n(\mathbf{r})\phi_m(\mathbf{r})$ and use a set of auxiliary basis functions $\zeta_\mu(\mathbf{r})$ to fit these orbital pairs,

$$\phi_n(\mathbf{r})\phi_m(\mathbf{r}) \approx \sum_{\mu=1}^{N_\mu} \zeta_\mu(\mathbf{r}) C_{nm}^{\mu}, \tag{15}$$

where the required number of auxiliary basis functions N_μ for accurately representing the orbital pairs is expected to be small and scale as $O(N)$ and C_{nm}^{μ} are fitting coefficients. With the approximation given in Eq. (15), one can calculate integrals $(kl|nm)$, which contribute to the elements of $\mathbf{C}$ and $\mathbf{D}$, with the following equations:

$$(kl|nm) \approx \sum_{\alpha=1}^{N_\mu}\sum_{\beta=1}^{N_\mu} (\alpha|\beta) C_{kl}^{\alpha} C_{nm}^{\beta} \tag{16}$$

$$(\alpha|\beta) = \int \frac{\zeta_\alpha(\mathbf{r})\zeta_\beta(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'. \tag{17}$$

These methods reduce four-center integrals to two-center integrals and also factorize $\mathbf{C}$ and $\mathbf{D}$ as products of small

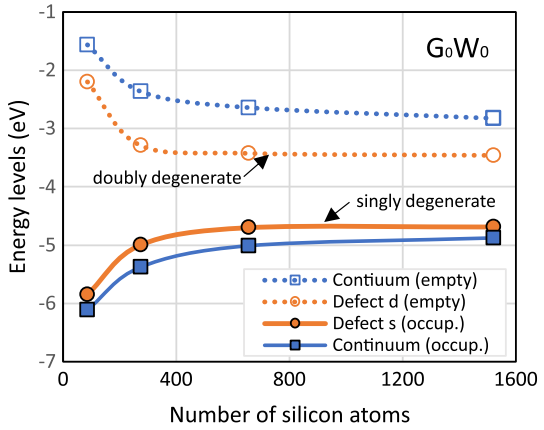

FIG. 2. Evolution of "continuum" states and silicon-vacancy defect states in different-sized silicon clusters.

matrices to accelerate the matrix-vector products. Here we used the interpolative separable density fitting (ISDF) method to efficiently construct low-rank approximations of orbital pairs [13,62,63]. Additionally, one can further exploit the point-group symmetries to make the Casida matrix $\mathbf{C}$ block diagonal and simplify the calculation of matrix-vector products [64].

Combined with the ISDF method [13], our method is efficient and enables large-scale G_0W_0 computations with modest computing resources. To demonstrate the efficiency of our method, we performed calculations for hydrogen-passivated silicon clusters. Silicon clusters have attracted research interest as prototypical semiconducting clusters for studying the fundamental physical properties of zero-dimensional systems [65] and their applications in many fields [66–69]. Defects in passivated silicon nanocrystals can introduce midgap defect levels as potential sources of photoluminescence [70,71], while their electronic structures are rarely studied by GW calculations. We computed the defect energy levels of charge-neutral silicon vacancies in silicon clusters of different sizes. The ground state of a silicon vacancy has zero net spin. Different from

TABLE I. The running time t_{wall} and the number of compute nodes N_{node} for calculating the GW quasiparticle energy of one quasiparticle state. Each compute node has 64 cores and 4 graphic processing units (GPU). t_{wall} includes the running time for performing the ISDF method and computing $\Sigma^{\text{GW}}(\omega)$ using the Lanczos method. $N_{\text{iter}} = 8$ and $g = 7$ are used for Lanczos iterations and polynomial functions, respectively.

Nanocluster	N_v	$N_c + N_v$	N_μ	N_{node}	t_{wall} (hr)
$Si_{86}H_{76}$	210	1730	7000	1	0.02
$Si_{274}H_{172}$	634	5200	20 000	2	0.3
$Si_{452}H_{228}$	1018	8200	32 000	2	0.7
$Si_{656}H_{300}$	1462	12 000	48 000	2	1.5
$Si_{1522}H_{524}$	3306	27 000	108 000	10	8.5
$Si_{1947}H_{604}$	4196	33 400	133 600	20	9.2

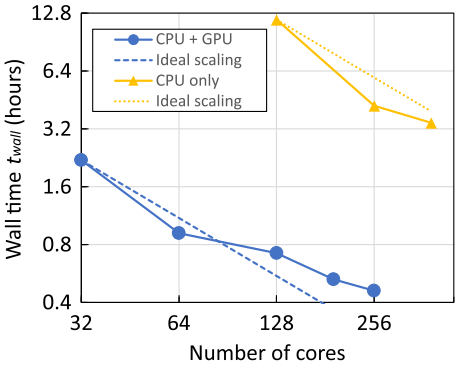

FIG. 3. The wall time for computing the GW quasiparticle energy of one state of the $Si_{452}H_{228}$ cluster with different numbers of CPU cores and GPUs (Nvidia A100). Every computer node has an EPYC 7763 CPU with 64 cores. For calculations accelerated with GPUs, every 16 CPU cores share 1 GPU processor.

nanodiamondoids, where surface states are located in the gap, the surface states of silicon nanoclusters are mixed with continuum states and the midgap states originate from defects. In the single-particle level, an occupied singlet and a pair of unoccupied doubly degenerate defect states are located inside the gap [72]. As shown in Fig. 2, when the size of silicon clusters increases, the energies of defect states evolve at a similar rate as the continuum states. For the $Si_{1522}H_{524}$ cluster, the band gap of continuum states is around 2.3 eV, still far from the bulk silicon band gap of 1.1 eV. We also computed the HOMO-LUMO gap of nondefective silicon nanocrystals, and our results agree well with previous calculations [37,73] (see Sec. 3 in the Supplemental Material [28] for more details).

The main calculation parameters and required computation resources for these calculations are shown in Table I. Notably, only two computing nodes are required for $Si_{656}H_{300}$. For the largest system, $Si_{1953}H_{604}$ with a diameter of around 4 nm, we used 20 nodes to accomplish the full-frequency GW calculation. The computational cost of our algorithm has a theoretical scaling of $O(N^4)$. In the benchmarks of silicon clusters, we observe a practical scaling of roughly $O(N^{2.3})$ for systems with less than 600 silicon atoms (see Sec. 4 of the Supplemental Material [28] for a detailed analysis of the computational costs). As shown in Fig. 3, we compared the running time for full-frequency GW calculations of $Si_{453}H_{228}$ using different numbers of nodes. For our Lanczos-based method, the most time-consuming steps are matrix-matrix and matrix-vector multiplications, which are suitable for massive parallelization and acceleration with GPUs in heterogeneous supercomputers. Figure 3 demonstrates the reasonably good strong scaling with computation resources. When the calculations are accelerated with GPUs, the speed-up factors compared to CPU-only calculations are around 20.

In summary, a full-frequency GW formalism based on a Lanczos method is proposed to realize efficient modeling of hundreds of atoms with modest resources. This method can be used for highly efficient full-frequency GW calculations of large finite systems, such as semiconductor quantum dots and ligand-protected superatomic clusters with a few hundred atoms. Our method can also facilitate the construction of computational databases with quasiparticle-energy data, which were challenging to accomplish with limited computational costs before. This method is ready to generalize to extended systems, for which complex-valued wave functions are required. If the Tamm-Dancoff approximation is used (i.e., setting matrix $\mathbf{B} = 0$ in the RPA Casida matrix) for extended systems, then the calculation is greatly simplified as only a Hermitian matrix $\mathbf{A}$ remains, and a standard Lanczos algorithm for the Hermitian matrix can be used. On the other hand, if RPA is used, then a Lanczos-based method designed for pseudo-Hermitian matrices [34,36,74] can be adopted.

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*zhaojj@dlut.edu.cn
†jrc@utexas.edu

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