

A time-dependent semiempirical approach to determining excited states

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We study a time-dependent semiempirical method to determine excitation energies, TD-PM3. This semiempirical method allows large molecules to be treated. A Linear-response Chebyshev approach yields the TD-PM3 spectrum very efficiently. Spectra and excitation energies were tested by comparing it with the results obtained using TD-DFT (Time Dependent-Density Functional Theory), using both small and large basis sets. They were also compared to PM3-CI, Time Dependent-Hartree Fock using the STO-3G basis set, and to experiment. TD-PM3 results generally match better the large-basis set calculations than the small-basis TD-DFT do; excitation energies are almost always accurate to within about 20% or less, except for a few small molecules. Accuracy improves as the molecules get larger. © 2010 American Institute of Physics.

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I. INTRODUCTION

Semiempirical methods have an important role in large scale simulations, allowing treatment of very large systems.^{1,2} Traditionally, semiempirical methods have been mostly used for time-independent ground-state simulations. However, with the rising interest in excited state dynamics, and the advent of large scale iterative computational methods, a natural question arises whether semiempirical time-dependent and/or iterative methods can be as useful for dynamics and for excited states. At present there are several semiempirical methods which have been used for excited-state dynamics. One is time-dependent tight-binding DFT,^{4,5} a method which bridges DFT (Density Functional Theory) and semiempirical tight binding^{6,7} in order to also treat systems such as organic molecules and biological molecules with atoms of different electronegativities, rather than the solid-state systems that tight binding has been generally used for. The other approach is to use a semiempirical MO-CI (molecular orbital-configuration interaction) method.⁸⁻¹⁰ This involves using a semiempirical program such as PM3 or MNDO along with a CI (configuration interaction) calculation such as CI singles or CI doubles in order to get single or double excited states.

A decade ago some interest has also risen in using time-dependent methods for polymeric systems. It was also realized that a Krylov subspace approach could be used to turn the time-dependent equation into a linear-response equation with an easily calculated action of a time-independent Liouville operator.¹² Here, we systematically investigate the PM3 approach using a Chebyshev framework of polynomial expansion of linear-response time-dependent density methods.^{14,15} We examine such an approach for a collection of small molecules, showing that even for small systems the excitation energies are quite accurate. The resulting approach is therefore very efficient numerically compared with direct

real time propagation since no time-dependent propagation is needed and the results are calculated directly in frequency space, iteratively, without any matrix diagonalization.

Conceptually, PM3 may seem unnatural as a time-dependent method, as it has been parametrized for ground states. However, it is known that linear-response time-dependent methods tend to have surprisingly good accuracies.¹⁴⁻¹⁷ The formal reason is that much of the effects which are missing in time-independent descriptions are just the polarization of the electron cloud (due to the Hartree terms) and a time-dependent treatment automatically takes those into account. [Formally, a time-dependent treatment takes the RPA (random phase approximation) diagrams into account.] We therefore examine here a straightforward application of PM3 to excited-state studies, and, indeed, find that the method is surprisingly accurate. Specifically, we show below that even without any parameter tweaking, a linear-response PM3 approach yields excitation energies which are often five times more accurate than the time-independent highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap, and are generally accurate to within 10%–20%.

The paper is arranged as follows. Section II reviews PM3 and linear response. Section III shows results, and conclusions follow in Sec. IV.

II. THEORY

A. PM3 equations

PM3 is an acronym for the modified neglect of diatomic orbital method-parametrized model 3 or MNDO-PM3. This model makes several assumptions in order to make its calculations feasible and efficient. It only treats the valence electrons of an atom, in a minimal basis, and approximates its inner shell electrons and the rest of its nucleus as a fixed core.

The electronic energy is calculated using

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$$E = \frac{1}{2} \sum_{ij} P_{ij} (H_{ij} + F_{ij}). \quad (1)$$

Here, P is the density matrix; H is the core Hamiltonian matrix, which includes the usual core Hamiltonian together with a dipole term

$$H_{ij} = H_{0,ij} + \mathbf{E} \cdot \mathbf{D}_{ij}, \quad (2)$$

due to any external electric fields, E (as will be important for the linear response evolution below), D is the electric dipole matrix, and F is the Fock matrix. The basis set for the matrices is composed of the valence shell atomic orbitals of each atom in the molecule.

The equations used to calculate the core Hamiltonian matrix and the Fock matrix are detailed by Stewart, Dewar, and Thiel¹⁹⁻²¹ and are briefly described below. We use the close-shell version, since if the ground state is made from closed-shell orbitals, it is sufficient to consider only the closed-shell equations for singlet-singlet transitions.

The core Hamiltonian matrix is composed of one-electron terms and is calculated by

$$H_{\mu\mu} = U_{\mu\mu} + \sum_B V_{\mu\mu,B}, \quad (3)$$

$$H_{\mu\nu} = \sum_B V_{\mu\nu,B}, \quad (4)$$

$$H_{\mu\lambda} = \frac{1}{2} (\beta_\mu^A + \beta_\lambda^B) S_{\mu\lambda}, \quad (5)$$

where the symbols are defined as follows.

First, here and in the following, μ and ν correspond to matrix elements pertaining to atomic orbital in atom A . The subscripts λ and σ denote atomic orbitals in an atom B which is different from atom A .

$U_{\mu\mu}$ is the sum of the kinetic energy of the electron in orbital μ and the potential energy of the attraction between the electron and the core of the atom in which this orbital resides. This parametrized term is determined by fitting several of its theoretical valence energies against the corresponding spectroscopic results.

$V_{\mu\nu,B}$ is the potential energy of the attraction between the electron in atom A and the core of atom B and is calculated by evaluating the two center integral representing the repulsion interactions between the charge distribution of the atomic orbitals represented by μ and ν in atom A and a purely spherical (s-type) charge distribution in atom B which approximates the core of atom B .

The β 's are parameters specific to the atom and the type of atomic orbital, i.e., whether it is s or p (there have been extensions to d- and higher order orbitals, but for most applications s and p orbitals suffice).

Finally, $S_{\mu\nu}$ is an element from the overlap matrix calculated from the overlap integrals of the individual minimal basis Slater orbitals. Next, we turn to the Fock matrix in a static field. It is composed of the core Hamiltonian and two-electron terms, the open shell equations for the alpha (spinup) Fock matrix are

$$F_{\mu\mu}^\alpha = H_{\mu\mu} + \sum_\nu^A [P_{\nu\nu}^{\alpha+\beta} (\phi_\mu^A \phi_\mu^A, \phi_\nu^A \phi_\nu^A) - P_{\nu\nu}^\alpha (\phi_\mu^A \phi_\nu^A, \phi_\mu^A \phi_\nu^A)] + \sum_B \sum_{\lambda,\sigma} P_{\lambda\sigma}^{\alpha+\beta} (\phi_\mu^A \phi_\mu^A, \phi_\lambda^B \phi_\sigma^B), \quad (6)$$

$$F_{\mu\nu}^\alpha = H_{\mu\nu} + 2P_{\mu\nu}^{\alpha+\beta} (\phi_\mu^A \phi_\nu^A, \phi_\mu^A \phi_\nu^A) - P_{\mu\nu}^\alpha [(\phi_\mu^A \phi_\nu^A, \phi_\mu^A \phi_\nu^A) + (\phi_\mu^A \phi_\mu^A, \phi_\nu^A \phi_\nu^A)] + \sum_B \sum_{\lambda,\sigma} P_{\lambda\sigma}^{\alpha+\beta} (\phi_\mu^A \phi_\nu^A, \phi_\lambda^B \phi_\sigma^B), \quad (7)$$

$$F_{\mu\lambda}^\alpha = H_{\mu\lambda} - \sum_\nu^A \sum_\sigma^B P_{\nu\sigma}^\alpha (\phi_\mu^A \phi_\nu^A, \phi_\lambda^B \phi_\sigma^B). \quad (8)$$

Here, φ represents the atomic orbitals of the specified atom. The terms in parentheses composed of atomic orbitals in the same atom A are the one-center two-electron repulsion integrals due to exchange and Coulomb forces between two electrons in different atomic orbitals but in the same atom. These are parametrized specifically to each atom using experimental data.

The terms in parentheses composed of atomic orbitals from two different atoms, A and B , are the two-center two-electron repulsion integrals due to the repulsion forces between two electrons in two different atoms. (All three- and four-center integrals are neglected.) The two-center integrals were calculated using the method and equations by Dewar and Thiel,²¹ where the interaction between orbitals on different atoms is approximated from electrostatic moments.

As the equations above show, a trait of semiempirical methods is the simplification of the Hamiltonian by replacing some of the terms with parameters and equations obtained by deriving them from and fitting them against experimental results and data.^{1,2,23-26}

The first stage in the simulation is completed by iteratively preparing the ground-state Fock and density matrices P_0 , F_0 fulfilling

$$P_0 = \theta(\mu - F_0(P_0)), \quad (9)$$

where we introduced the chemical potential and step function. Standard sparse-matrix methodologies can be used to efficiently do the Hartree-Fock (HF) iterations for large systems. The ground-state density matrix is then used as an input to the time-dependent stage.

B. Time-dependent PM3

After the electronic energy converges, the time-dependent response is mostly simply calculated in real time from evolving the time-dependent equation

$$i \frac{\partial P}{\partial t} = [F(P(t)), P(t)]. \quad (10)$$

The time dependence is induced by a simple addition of an electric field delta-function (in time) perturbation to the initial Fock matrix, i.e., using

$$\mathbf{E}(t) = \delta(t)\mathbf{E}_0. \quad (11)$$

After the delta-function perturbation ends, the density matrix (denoted as P^{start} to distinguish it from the original density matrix, P_0) takes the form

$$P^{\text{start}} = P_0 - i[\mathbf{E} \cdot \mathbf{D}, P_0]. \quad (12)$$

P^{start} is used as the initial condition to the time-dependent propagation.

A full time-dependent linear propagation is often expensive, although there has been considerable progress in direct real time propagation (see, e.g., Ref. 27 and references therein). Since the vast majority of applications will be concerned with linear response, we used here a more efficient iterative Chebyshev approach (see Refs. 14 and 15). This approach is different from the more commonly used frequency-based linear-response approach used by Casida^{28,29} and others^{16,17,30} in that it processes all frequencies at once without matrix diagonalization. Using this approach allows for the excitation energies to be found simply from the Fourier transform of the propagation of the density matrix over time. For greater efficiency, a similar iterative approach to that developed in Refs. 14 and 15 but which extracts the spectrum directly in frequency space was used here. This approach will be explained below.

C. Manifestly linear evolution equations

The linear response approach to PM3 and density matrices in general is even simpler than the previously introduced wave function approach.^{14,15}

We define the deviation between the actual and ground-state density matrix as

$$W(t) = P(t) - P_0. \quad (13)$$

Defining $F_0 = F(P_0)$ and using $[F_0, P_0] = 0$, we expand the evolution equation [Eq. (10)] for the density matrix ignoring terms of order W^2 ,

$$i \frac{\partial}{\partial t} W(t) = [F(W(t) + P_0) - F_0, P_0] + [F_0, W(t)], \quad (14)$$

a form which is linear in W for small enough deviations. The $-F_0$ term in Eq. (14) is important to impose linearity in the typical case where numerically $[F_0, P_0]$ is small but non-vanishing. The linearity can be further imposed by scaling through a small constant, denoted by g , resulting at

$$\frac{\partial}{\partial t} W(t) = LW, \quad (15)$$

where the Liouville superoperator is defined as

$$LW = \frac{-i}{g} [F(gW(t) + P_0) - F_0, P_0] - i[F_0, W] \quad (16)$$

[in practice we found that a variable g , equal to a small number (e.g., 10^{-5}) times the norm of W , leads to uniformly stable results].

The initial density matrix is then obtained by applying a delta-function electric field perturbation, which results in a starting density of

$$W^{\text{start}} = P^{\text{start}} - P^0 = -i[\mathbf{E} \cdot \mathbf{D}, P_0]. \quad (17)$$

The linear evolution equation is then solved by the iterative Chebyshev algorithm. Formally, the time-dependent propagation is represented as

$$\begin{aligned} W(t) &= e^{Lt} W^{\text{start}} = \sum_n (2 - \delta_{n0}) J_n(t\Delta) T_n\left(\frac{L}{\Delta}\right) W^{\text{start}} \\ &= \sum_n (2 - \delta_{n0}) J_n(t\Delta) \zeta_n, \end{aligned} \quad (18)$$

where Δ is a parameter essentially equaling to (or somewhat larger than) the typical energy range in the Fock operator, and we introduced the Bessel function and the modified Chebyshev series, formally defined as

$$\zeta_n = T_n\left(\frac{L}{\Delta}\right) W^{\text{start}}, \quad (19)$$

where T_n are modified Chebyshev operators defined as

$$T_n(x) = i^{-n} \text{acos}(ix). \quad (20)$$

In practice, the series is evaluated as

$$\begin{aligned} \zeta_0 &= W^{\text{start}}, \\ \zeta_1 &= \frac{LW^{\text{start}}}{\Delta}, \end{aligned} \quad (21)$$

$$\zeta_n = 2 \frac{L\zeta_{n-1}}{\Delta} + \zeta_{n-2}.$$

Note that each element ζ_n is itself a density matrix of the same dimensions as P_0 .

In practice we are typically interested in the absorption spectrum. For that, we need the time-dependent dipole,

$$\mathbf{d}(t) = \text{Tr}(\mathbf{D}W(t)). \quad (22)$$

The dipole will yield the absorption cross section defined as

$$B(\omega) = \omega \text{Im}(\mathbf{E}_0 \cdot \mathbf{d}(\omega)), \quad (23)$$

where

$$\mathbf{d}(\omega) = \frac{1}{2\pi} \int_0^\infty e^{-t^2 a^2/2} e^{i\omega t} \mathbf{d}(t) dt.$$

Noticing that W^{start} is purely imaginary, we get

$$\begin{aligned} \text{Im } \mathbf{d}(\omega) &= \frac{1}{2\pi} \text{Im} \int_0^\infty \text{Tr}(\mathbf{D} \cdot e^{i\omega t} e^{Lt} W^{\text{start}}) dt \\ &= \text{Tr}(\mathbf{D} \cdot \delta(iL - \omega) W^{\text{start}}) dt, \end{aligned} \quad (24)$$

where the delta function is evaluated by a Chebyshev iterative algorithm. In practice, it is Gaussian broadened and defined as

$$\delta(iL - \omega) = \frac{1}{\sqrt{2\pi}a} \exp\left(-\frac{(iL - \omega)^2}{2a^2}\right), \quad (25)$$

where a is a frequency-width parameter; we then follow with the expression

TABLE I. Lowest excitation energies of small molecules obtained using TD-PM3 and various methods (energies in eV; TD-DFT using B3LYP).

Molecule	Transition	TD-PM3	TD-DFT aug-cc-pvtz	TD-DFT 3-21G	TD-HF STO-3G	PM3-CI	Band gap	Expt.
H ₂	$\Sigma_u: \sigma \rightarrow \sigma^*$	9.96	11.74	15.76	15.07	10.25	20.86	11.19 ^a
HF	$\Sigma_g: n \rightarrow \sigma^*$	8.66	9.33	9.57	13.11	8.59	19.75	10.35 ^b
F ₂	$\Pi_u: \pi^* \rightarrow \sigma^*$	4.85	5.26	5.29	7.16	4.52	15.53	4.4 ^c
CO	$\Pi: \sigma \rightarrow \pi^*$	7.56	8.60	8.43	8.59	7.01	14.03	8.55 ^d
CH ₄	$T_2: \sigma \rightarrow \sigma^*$	8.76	9.63	13.43	24.03	8.59	17.88	9.7 ^d
C ₂ H ₄	$B_{3u}: \pi \rightarrow 3s$	8.26	6.69	10.11	15.37	8.43		7.11 ^d
	$B_{1u}: \pi \rightarrow \pi^*$	5.76	7.47	8.76	11.41	6.65	11.72	7.60 ^d
CH ₂ O	$B_2: n \rightarrow 3s$	5.56	6.48	9.15	18.65	5.57	11.37	7.11 ^d

^aReference 3.^bReference 13.^cReference 18.^dReference 22.

$$\frac{1}{\sqrt{\pi a}} \exp\left(-\frac{(iL - \omega)^2}{a^2}\right) = \sum_n T_n\left(\frac{L}{\Delta}\right) f_n(\omega), \quad (26)$$

where $f_n(\omega)$ are frequency dependent coefficients (evaluated in the Appendix). The equations above result in Gaussian broadened density matrices,

$$W(\omega) \equiv \frac{1}{\sqrt{\pi a}} \exp\left(-\frac{(iL - \omega)^2}{a^2}\right) W^{\text{start}} = \sum_n f_n(\omega) \zeta_n, \quad (27)$$

so that finally,

$$B(\omega) = \omega \sum_n f_n(\omega) \mathbf{D} \cdot \mathbf{R}_n, \quad (28)$$

where the residues

$$\mathbf{R}_n = \text{Tr}\left(\mathbf{D} T_n\left(\frac{L}{\Delta}\right) W^{\text{start}}\right) = \text{Tr}(\mathbf{D} \zeta_n) \quad (29)$$

are each a length-three vector.

The final result is therefore very simple, as in practice the calculation of the absorption spectrum amounts to the calculation of Chebyshev series, and while it is evaluated the residues need to be collected. Then, for each desired damping parameter, the spectrum is calculated from Eq. (28).

The number of Chebyshev terms in our simulations is about $4\Delta/a$, which for typical spectra yields several thousand terms. There are several methods for expediting convergence of a Chebyshev series and these should yield up to an order of magnitude improvement in the number of terms (and even more for isolated spectra) as will be investigated in future studies.

III. SIMULATIONS

A. Overview

For this test study, several small representative molecules were first used: dihydrogen, hydrogen fluoride, difluoride, carbon monoxide, methane, ethene, and formaldehyde. These molecules are well represented by established methods such as DFT and TD-DFT (Time Dependent-Density Functional Theory) with standard functionals. In addition, the program was tested on the following aromatics, benzene, naphthalene, anthracene, tetracene, and pentacene, in order to determine its accuracy as the molecules increase in size.

The first step in the simulations is the construction of the ground-state density and Fock matrices by established methods. The electric dipole perturbation is then added and the density matrix is iterated over time using Eq. (14).

Next, Eq. (28) is applied; typically we use a few thousand terms for convergence (indicated by a totally positive spectrum without any negative parts which will be artifacts of lack of convergence). The width parameters taken were

$$a = 0.05 \text{ eV}, \quad \Delta = 50 \text{ eV}, \quad (30)$$

where a was chosen to yield well-isolated peaks in the spectra, while Δ was chosen to ensure convergence of the Chebyshev expansion (the only requirement on Δ is that it needs to be higher than the half width of the spectrum of L ; the simplest way to ensure this requirement is by empirically choosing a low enough where the expansion still converges).

From the spectrum we extract the lowest excitation energies. For the test calculations, we first checked our time-independent PM3 results against that of established PM3 routine in Gaussian, obtaining essentially identical results. The HOMO-LUMO gap was then reproduced by direct diagonalization of the time-independent Fock.

The PM3 program in the molecular package MOPAC (Ref. 20) was first used to optimize the geometry of the small molecules. The DFT program in the molecular package Q-CHEM (Ref. 31), was ultimately used to optimize the geometry using the B3LYP functional with the 6-311G** basis set. The excitation energies were then found for the molecules in their optimized geometry using the resulting linear-response time-dependent PM3 and also the TD-DFT program in Q-CHEM.

B. Results

Table I shows the lowest allowed singlet vertical excitations with significant oscillation strengths (generally above 10^{-4} a.u.) calculated using the time-dependent PM3 program by the TDDFT module in Q-CHEM using two basis sets, large (aug-cc-pvtz) and small (3-21G), the PM3-CI program in MOPAC with five states, and experimental values. In all cases we compared closed-shell simulations, where the ground-state density matrix is equal for both spins. There are some weak transitions which have very little overlap with symmetric closed-shell transitions which are therefore not

TABLE II. Lowest excitation energies of aromatics obtained using TD-PM3 and various methods (energies in eV; TD-DFT using B3LYP).

Molecule	Transition	TD-PM3	TD-DFT 6-311G**	PM3-CI	Band gap	Expt. ^a
Benzene	1E _{1u} : $\pi \rightarrow \pi^*$	5.56	7.34	6.25	10.12	6.9
Naphthalene	1B _{2u} : $\pi \rightarrow \pi^*$	3.45	4.41	4.09	8.34	4.45
	2B _{3u} : $\pi \rightarrow \pi^*$	4.85	6.03	5.42		5.89
Anthracene	1B _{2u} : $\pi \rightarrow \pi^*$	2.95	3.24	3.51	7.18	3.31
	1B _{3u} : $\pi \rightarrow \pi^*$	4.35	5.27	4.92		4.92
Tetracene	1B _{2u} : $\pi \rightarrow \pi^*$	2.55	2.47	3.10	6.39	2.63
	2B _{3u} : $\pi \rightarrow \pi^*$	3.95	4.71	4.58		4.51
Pentacene	1B _{2u} : $\pi \rightarrow \pi^*$	2.25	2.17	2.95	5.82	2.12
	2B _{3u} : $\pi \rightarrow \pi^*$	3.75	4.63	3.99		4.10

^aReference 11.

shown, such as a weak A₂ transition in TDDFT and experiment around 4.0 eV for CH₂O.

The TDDFT calculations used the hybrid exchange and correlation functional B3LYP. Generally, the larger the basis set the more accurate is the result obtained by a TDDFT calculation. Accuracy can also be improved by choosing a basis set that includes diffuse and valence polarization functions. While the large basis set will be more accurate, it is limited in practice for large systems due to the numerical cost; this was the reason we compared PM3 to smaller basis sets.

In practice, the lowest excitation energies were obtained using the time-dependent iterations and the graphs produced and taking the lowest peak (and as mentioned, more efficient approaches can be envisioned for extracting the gap from the Chebyshev series if only the low energy spectrum is desired). The peaks give energies that are allowed and have significant oscillator strengths. The transitions were determined by observing the direction of the dipole applied on the molecule.

Table I shows mixed quality results. The TD-PM3 results were much better than the band gap and in many cases better than TD-DFT with the 3-21G basis set. They were generally about 20% lower than the more accurate large-basis (aug-cc-pvtz) TD-DFT results as well as the experimental results. The main exception is C₂H₄, where the true lowest state with significant dipole strength is a transition to $\pi \rightarrow 3s$ transition, while TD-PM3 predicts a $\pi \rightarrow \pi^*$ as lower.

Table II compares TD-PM3, TD-DFT, and PM3-CI for a series of aromatic rings. PM3-CI is accurate for the smaller aromatics, but for the fixed number $n=5$ of configurations used here, it deteriorates, indicating that more configurations are needed for larger systems. The TD-PM3 results improved (relatively and absolutely) as the molecules got bigger.

IV. DISCUSSION AND CONCLUSIONS

Our results indicate that a time-dependent application of a semiempirical method (in this case PM3 but the results should be of general validity) is useful for large molecules. The results, especially for larger molecules, were surprisingly accurate, especially considering that we did not reoptimize the parameters. The PM3 parameters that were employed have been optimized previously to yield accurate

ground-state properties, and this work shows that these same parameters lead to surprisingly accurate excitation energies when used in a TD-PM3 scheme.

The timings on the method are interesting. The nonoptimized TDPM3 code was about 200–150 times faster than the large-basis TDDFT code. PM3-CI with $n=5$ configurations was faster significantly (more than an order of magnitude) than TD-PM3, especially since at present TD-PM3 scales like the cube of the number of orbitals because of the matrix multiplication ($[F, H]$) in the time evolution. TD-PM3 is clearly not a method for small molecules, but rather for large systems for two purposes: real time dynamics, or for spectral applications, once the method is made numerically more efficient, especially by accounting for the sparsity in the application of F on H . Numerical efficiency and its improvements will be discussed in more details in future publications.

Further improvements can still be made. PM3 equations and parameters for d-orbital atoms have already been developed^{32,33} so this program can be revised to include d-orbital atoms. Another improvement is to modify the parameters used in the PM3 program. Since the parameters used are based on the ground state of the molecule, in principle they could be modified to yield better spectra while retaining reasonable accuracy for ground-state properties. In a future publication we discuss the application of these concepts to more general quantities than absorption, as well as more rapid extraction of the frequency information.

In addition, the same concepts and methods implied here can be applied directly to other semiempirical methods such as INDO/S (Intermediate Neglect of Differential Overlap/Screened Approximation), which has been popular for computing vertical excitation energies; future publications will examine where TD-INDO/S will outperform TD-PM3.

To conclude, our results show that a time-dependent application of a semiempirical method should be useful for large systems, where highly quantitative results are not needed but accuracies of $\sim 20\%$ are desired. Further numerical developments to improve the scaling should make the method applicable for a range of large scale problems.

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APPENDIX: FREQUENCY DEPENDENT EXPANSION COEFFICIENTS

The calculation of the coefficients in Eq. (26) is straightforward and well known, and is presented here for completeness, since we use the modified Chebyshev polynomials rather than the regular ones [defined as in Eq. (20) without the i 's]. A general function of $iL - \omega$ is written as

$$f(iL - \omega) = \sum_n T_n\left(\frac{L}{\Delta}\right) f_n(\omega). \quad (\text{A1})$$

Using the definition of the modified Chebyshev operator, we have

$$\int_0^{2\pi} T_n(i^{-1} \cos(\theta)) T_m(i^{-1} \cos(\theta)) d\theta = \frac{2\pi}{2 - \delta_{n0}} \delta_{nm}, \quad (\text{A2})$$

so that

$$\begin{aligned} f_n(\omega) &= \frac{(2 - \delta_{n0})}{2\pi} \int_0^{2\pi} \cos(n\theta) f(\Delta \cdot \cos \theta - \omega) d\theta \\ &= \text{Re} \frac{(2 - \delta_{n0})}{2\pi} \int_0^{2\pi} e^{in\theta} f(\Delta \cdot \cos \theta - \omega) d\theta, \end{aligned} \quad (\text{A3})$$

where the last step is valid for real functions. Therefore, the coefficients are easily obtained by a simple Fourier transform.

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