Real Time Propagation of the Exact Two Component Time-Dependent Density Functional Theory

Joshua J. Goings, Joseph M. Kasper, Franco Egidi, Shichao Sun, Xiaosong Li*

Department of Chemistry, University of Washington, Seattle, WA 98195

email: `xsli@uw.edu`

Abstract

We report the development of a real time propagation method for solving the time-dependent relativistic exact two-component density functional theory equations (RT-X2C-TDDFT). The method is fundamentally non-perturbative and may be employed to study nonlinear responses for heavy elements, which require a relativistic Hamiltonian. We apply the method to several Group 12 atoms as well as heavy-element hydrides, comparing with the extensive theoretical and experimental studies on this system, which demonstrates the correctness of our approach. Because the exact two-component Hamiltonian contains spin-orbit operators, the method is able to describe the non-zero transition moment of otherwise spin-forbidden processes in non-relativistic theory. Furthermore, the two-component approach is more cost effective than the full four-component approach, with similar accuracy. The RT-X2C-TDDFT will be useful in future studies of systems containing heavy elements interacting with strong external fields.

1 Introduction

Relativistic effects are known to be important for the description of heavy elements. For example, the yellow color of gold and the fact that mercury is liquid at room temperature are both the result of including relativistic corrections to the non-relativistic Schrödinger equation.[1–3] The proper starting point for the description of molecular relativistic effects is the Dirac-Hartree-Fock/Dirac-Kohn-Sham four-component Hamiltonian. However, because of its four-component nature, the Dirac-Hartree-Fock/Dirac-Kohn-Sham Hamiltonian quickly becomes an expensive Hamiltonian to use in realistic calculations involving heavy elements. Furthermore, there is additional work in the full four-component calculations in that the Dirac equation also contains negative energy solutions corresponding to positronic solutions.[1,2] These are often of little interest to chemical applications. Therefore, much effort has been spent to decouple the four-component equations into two-component electronic and positronic equations, which retain the physical relativistic effects of the full four-component equations, but at reduced cost.[1,2]

One of the most promising two-component methods in recent times has been the introduction of the exact two-component transformation (X2C).[4–13] X2C approximately decouples the parent four-component Hamiltonian into a reduced dimension electronic two-component Hamiltonian. For one-electron systems, X2C will recover the exact four component eigenspectrum of the underlying four-component Dirac equation. Other two-component methods of note are the normalized elimination of the small component (NESC),[14–18] the Douglas-Kroll-Hess transformation,[19–22] and the zeroth-order-regular approximation (ZORA).[11,23–25] Relations between these methods have been detailed in Ref. 12.

Given the success of such relativistic Hamiltonians for ground state properties, it is natural to consider the effectiveness of their extension to excited state properties, such as optical absorption spectra. In particular, relativistic effects are necessary to qualitatively describe excited states split by spin-orbit and spin-spin interactions. Both four-component and two-component relativistic Hamiltonians have been successfully applied to the description of excited states using the linear response (LR) formalism.[26–37] However, the linear response formalism is fundamentally limited to system response of small, perturbative fields. If one desires to compute nonlinear response properties and the response of systems containing heavy elements in strong fields, it may be necessary to employ a real-time propagation approach[38–40] to the time-dependent relativistic equations.

Recently, a real-time (RT) propagation approach for the four-component Dirac-Kohn-Sham equations was presented.[41] The method was able to describe the response of strong fields to systems within a fully relativistic theory, and was able to describe spin-forbidden transitions and other unique relativistic aspects of optical absorption spectra. Unfortunately, because of the underlying four-component Hamiltonian, the solution of the equations is rather expensive. Here, we present a real-time propagation approach utilizing the time-dependent two-component X2C Hamiltonian. The solution of these equations provides an economical approach to describing the response of systems containing heavy elements. We briefly describe the two component transformation and our real-time propagation scheme for two component Hamiltonians, based off our previous work propagating non-relativistic two-component equations.[40,42] We demonstrate the correctness of our approach by comparing with linear response two-component time-dependent density functional theory (TDDFT), as well as the four-component RT-TDDFT results. Finally, we look forward to the potential of real-time time-dependent X2C for strong fields and spin-dependent dynamics.

2 Theory

Here we briefly outline the exact two-component transformation, using atomic units. We follow the notation of Peng, *et al.*, as our implementation closely follows the X2C implementation outlined in their paper.[9] Bold formatting $\mathbf{M}$ indicates matrices in two-component (2c) space and for matrix representation of four-component operators we use the split notation for large (L) and small (S) components. In some cases, four-component (4c) matrices will be indicated by blackboard bold $\mathbb{M}$. Finally, sans-serif matrices M correspond to complex matrices in a basis set of spin-free functions. We refer interested readers to Ref. 9 for more details. The goal of X2C, as with most two-component methods, is to exactly decouple the large and small components of the four-component one-electron modified Dirac equation. X2C accomplishes this goal by exactly decoupling the one-electron Dirac equation represented in a restricted kinetically balanced basis, given as

$$\begin{pmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & (\frac{1}{4c^2}\mathbf{W}-\mathbf{T}) \end{pmatrix}\begin{pmatrix} \mathbf{C}_L^+ & \mathbf{C}_L^- \\ \mathbf{C}_S^+ & \mathbf{C}_S^- \end{pmatrix} = \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & \frac{1}{2c^2}\mathbf{T} \end{pmatrix}\begin{pmatrix} \mathbf{C}_L^+ & \mathbf{C}_L^- \\ \mathbf{C}_S^+ & \mathbf{C}_S^- \end{pmatrix}\begin{pmatrix} \epsilon^+ & \mathbf{0} \\ \mathbf{0} & \epsilon^- \end{pmatrix} \tag{1}$$

Here $\mathbf{V}$, $\mathbf{T}$, and $\mathbf{S}$ are the non-relativistic matrix representations of the one-electron potential energy operator ($\mathcal{V}$), the kinetic energy operator, and the overlap, respectively. $\mathbf{W}$, however, is the relativistic potential energy operator, represented as

$$W_{ij} = \langle \chi_i | \, \vec{\sigma} \cdot \vec{p} \, \mathcal{V} \, \vec{\sigma} \cdot \vec{p} \, | \chi_j \rangle \tag{2}$$

where $\vec{p}$ is the linear momentum vector and $\vec{\sigma}$ is the vector containing the Pauli spin operators. All the matrices are represented over two-component spinor functions, $\{\chi_i\}$. Finally, c is the speed of light and $\mathbf{C}$ and ϵ collect the wave function coefficients and orbital energies, respectively.

To decouple Eq. (1), we seek a unitary transformation $\mathbb{U}$ that block diagonalizes the 4c Dirac Hamiltonian into two, two-component equations. The decoupled equations will correspond to positive and negative energy states, and we seek solutions only to the positive energy solutions, which correspond to electronic solutions. Mathematically, we seek to find $\mathbb{U}$ such that

$$\tilde{\mathbf{H}} = \begin{pmatrix} \mathbf{U}^{LL,\dagger} & \mathbf{U}^{SL,\dagger} \end{pmatrix} \begin{pmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & (\frac{1}{4c^2}\mathbf{W}-\mathbf{T}) \end{pmatrix} \begin{pmatrix} \mathbf{U}^{LL} \\ \mathbf{U}^{SL} \end{pmatrix} \tag{3}$$

is satisfied. In the X2C method, the matrix representation of $\mathbb{U}$ is given by

$$\mathbb{U} = \begin{pmatrix} \mathbf{U}^{LL} & \mathbf{U}^{LS} \\ \mathbf{U}^{SL} & \mathbf{U}^{SS} \end{pmatrix} = \begin{pmatrix} \frac{\mathbf{I}}{\sqrt{\mathbf{I}+\mathbf{X}'^{\dagger}\mathbf{X}'}} & -\mathbf{X}'^{\dagger}\frac{\mathbf{I}}{\sqrt{\mathbf{I}+\mathbf{X}'\mathbf{X}'^{\dagger}}} \\ \mathbf{X}'\frac{\mathbf{I}}{\sqrt{\mathbf{I}+\mathbf{X}'^{\dagger}\mathbf{X}'}} & \frac{\mathbf{I}}{\mathbf{I}+\mathbf{X}'\mathbf{X}'^{\dagger}} \end{pmatrix} \tag{4}$$

which only holds in an orthonormal basis, denoted by the primes. The X2C method extracts a matrix representation of $\mathbf{X}'$ by solving the one-electron modified Dirac Hamiltonian in an orthonormal basis.

$$\mathbb{H}' \begin{pmatrix} \mathbf{C}^{+}_{L'} \\ \mathbf{C}^{+}_{S'} \end{pmatrix} = \begin{pmatrix} \mathbf{C}^{+}_{L'} \\ \mathbf{C}^{+}_{S'} \end{pmatrix} \epsilon^{+} \tag{5}$$

From the solution of Eq. (5), the explicit matrix expression for $\mathbf{X}'$ can be obtained from the wave function coefficients

$$\mathbf{X}' = \mathbf{C}^{+}_{S'} \cdot \left(\mathbf{C}^{+}_{L'}\right)^{-1} \tag{6}$$

Plugging Eq. (6) into Eq. (4) and generating the X2C Hamiltonian via Eq. (3) defines our transformation from 4-component to 2-component in the X2C method.

The extension to many electron systems corresponds to the same transformation in Eq. (3) but for the modified four-component Dirac-Hartree-Fock equation. In our implementation, we do not transform the matrix representation of the two-electron operator. This is equivalent to the Dirac-Coulomb approximation for the two-electron operator. We do however, include an empirical correction in the one-electron terms to account for the screening due to the two-electron terms.[43] Furthermore, the two-electron interactions depend on the X2C density, which generates some relativistic dependence to the two electron interaction.

$$\mathsf{F}^{\sigma\sigma'} = \mathsf{h}^{\sigma\sigma'} + \delta_{\sigma\sigma'}\mathsf{J}\left(\mathsf{P}^{\alpha\alpha} + \mathsf{P}^{\beta\beta}\right) - \theta\mathsf{K}\left(\mathsf{P}^{\sigma\sigma'}\right) - (1-\theta)\mathsf{V}^{\mathrm{DFT}}_{x}\left(\mathsf{P}^{\sigma\sigma'}\right) + \mathsf{V}^{\mathrm{DFT}}_{c}\left(\mathsf{P}^{\sigma\sigma'}\right) \tag{7}$$

Here h contains the transformed one-electron integrals, J contains the Coulomb integrals, and K contains the exchange integrals. σ denotes a spin-projection component, spin-up (α) or spin-down (β). $\mathsf{V}^{\mathrm{DFT}}_{x}$ and $\mathsf{V}^{\mathrm{DFT}}_{c}$ are the DFT exchange and correlation functionals, respectively. θ denotes a mixing parameter that mixes in a certain amount of Hartree-Fock exchange. For pure DFT θ is zero and for pure Hartree-Fock $\theta = 1$. (For pure Hartree-Fock we omit $\mathsf{V}^{\mathrm{DFT}}_{c}$ as well.)

Density functionals commonly developed for quantum chemical calculations are only formulated for systems with a collinear density for which the spin magnetization is oriented along the z axis at every point in space. Common exchange-correlation kernels only depend on $\mathsf{P}^{\alpha\alpha}$ and $\mathsf{P}^{\beta\beta}$ therefore, in order to use such functionals to describe systems with a non-collinear spin magnetization, the functional dependence must be reformulated to account for the presence of a non-zero magnetization oriented along the x and y directions, as well as their gradients (in the case of GGA functionals) in Eq. (7). The non-collinear XC kernel for 4c methods has been explored by Liu, *et al.*[26,32,33,44] We employ a recently reported formalism[45–48] that defines a set of auxiliary variables, detailed in Ref. 47, that take all magnetization components into account. This form has the advantage of exerting a non-zero local torque acting on the magnetization, while yielding a vanishing total torque, as expected from the exact functional.[49]

To propagate the X2C equations in time, we must consider the time-dependent version of the X2C Hamiltonian.

$$i\frac{\partial}{\partial t}\begin{pmatrix} \mathsf{P}^{\alpha\alpha}(t) & \mathsf{P}^{\alpha\beta}(t) \\ \mathsf{P}^{\beta\alpha}(t) & \mathsf{P}^{\beta\beta}(t) \end{pmatrix} = \left[\begin{pmatrix} \mathsf{F}^{\alpha\alpha}(t) & \mathsf{F}^{\alpha\beta}(t) \\ \mathsf{F}^{\beta\alpha}(t) & \mathsf{F}^{\beta\beta}(t) \end{pmatrix}, \begin{pmatrix} \mathsf{P}^{\alpha\alpha}(t) & \mathsf{P}^{\alpha\beta}(t) \\ \mathsf{P}^{\beta\alpha}(t) & \mathsf{P}^{\beta\beta}(t) \end{pmatrix}\right] \tag{8}$$

We integrate Eq. (8) with a modified midpoint and unitary transformation (MMUT) algorithm.[38,50,51] In the MMUT method, the time-evolution operator is a unitary transformation matrix $\mathbf{Q}(t_n)$ that is constructed from the eigenvectors $\mathbf{C}(t_n)$ and eigenvalues $\epsilon(t_n)$ of the X2C Hamiltonian matrix at time t_n:

$$\mathbf{C}^\dagger(t_n) \cdot \mathbf{F}(t_n) \cdot \mathbf{C}(t_n) = \epsilon(t_n) \tag{9}$$

and

$$\begin{aligned}\mathbf{Q}(t_n) &= \exp\left[-i \cdot 2\Delta t \cdot \mathbf{F}(t_n)\right] \\ &= \mathbf{C}(t_n) \cdot \exp\left[-i \cdot 2\Delta t \cdot \epsilon(t_n)\right] \cdot \mathbf{C}^\dagger(t_n)\end{aligned} \tag{10}$$

where Δt is the time step. Then, the density matrix is propagated from time t_{n-1} to t_{n+1} using the time-evolution operator $\mathbf{Q}(t_n)$:

$$\mathbf{P}(t_{n+1}) = \mathbf{Q}(t_n) \cdot \mathbf{P}(t_{n-1}) \cdot \mathbf{Q}^\dagger(t_n) \tag{11}$$

The MMUT method accounts for linear changes in the density matrix during the time step because it computes the X2C Hamiltonian matrix at the midpoint. MMUT is a symplectic integration scheme which allows for a large step size, while simultaneously controlling for numerical noise and integration errors.[38]

To excite all dipole-allowed electronic transitions, it is necessary to perturb Eq. (7) with an electric field along each real-space coordinate (e.g. x, y, z). This modifies the X2C Hamiltonian matrix such that

$$\mathbf{F}_{\mathrm{E}}(t) = \mathbf{F}(t) + \sum_{q=x,y,z} \kappa(t)\langle r_q\rangle \tag{12}$$

where $\mathbf{F}_{\mathrm{E}}(t)$ is the time-dependent X2C Hamiltonian matrix containing the external electric field, $\kappa(t)$ is the field strength at time t, and $\langle r_q\rangle$ are the atomic-orbital based length-gauge dipole integrals along component q. The electric dipole operator matrix $\langle r_q\rangle$ used in the propagation is subject to the X2C picture-change transformation. In the electric-dipole approximation in the length gauge, the electric field does not couple different spin components.[40,52] As a result, the X2C transformation matrix is invariant with respect to an external electric field perturbation. Therefore, the same X2C transformation matrix is used to transform the electric dipole operator matrix that goes into Eq. (12).

Because time is discretized, the perturbation corresponds to a step function lineshape lasting for only the initial time-step of width Δt, e.g.

$$\kappa(t) = \begin{cases} \kappa_{\max}, & 0 \leq t < \Delta t, \\ 0, & \text{else} \end{cases} \tag{13}$$

in this case, the discrete Fourier transform of $\kappa(t)$ will simply be $\kappa_{\max}$. One important caveat for including the electric dipole field in the X2C equations is that the atomic orbital electric dipole integrals must also be transformed using the transformation matrix in Eq. (4). This corrects for the so-called “picture-change” error in two-component methods that originates from transforming the four-component picture to the two-component picture.[53]

3 Results and Discussion

The real-time propagation of the X2C Hamiltonian was implemented in a locally modified copy of the developer's version of the Gaussian electronic structure program.[54] All calculations were performed using the SVWN5[55,56] density functional with the Sapporo-DKH3-DZP-2012 gaussian basis set including diffuse-*sp* functions.[57] The density functional and basis set were chosen in order to be able to compare with existing relativistic response theory implementations, which will be discussed below. After a ground state density optimization, each system was perturbed with an electric dipole delta pulse corresponding to a κ_{max} of 0.0001 au along each unique Cartesian axis. Each real-time calculation was propagated using a maximum time step of 0.0012 fs for at least 50 fs. Energy was conserved to at least 10^{-8} au. To accelerate the convergence of the Fourier transform, a Padé transformation scheme was utilized.[58] The electric dipole response was exponentially damped so as to give each peak a Lorentzian line shape with full-width half-max of 0.01 eV.

To obtain the optical absorption spectra, we take the Fourier transform of the time-dependent electric dipole moment $\mu(\omega)$ parallel to the polarization of the electric field perturbation κ. This corresponds to the frequency-dependent polarizability. The isotropic dipole strength function $S(\omega)$ is proportional to the imaginary component of the trace of the frequency dependent polarizability. That is to say,

$$S(\omega) \propto \sum_{\alpha=x,y,z} \text{Tr}\left[\omega \cdot \text{Im}\frac{\mu_\alpha(\omega)}{\kappa_\alpha}\right] \tag{14}$$

In order to test our implementation, we follow the pioneering four-component RT-TDDFT work of Repisky, *et al.*[41] and choose to study the excitation energies of three Group 12 atoms and two heavy-element hydrides. This allows us to compare not only with a four-component RT-TDDFT implementation, but also to compare with several four-component and two-component relativistic LR-TDDFT implementations.[26–30] Furthermore, there exist robust experimental data for these systems, which allows us to compare directly with experiment. For the heavy-element hydrides, TlH and AuH, experimental equilibrium geometries were used ($r_{Tl-H} = 1.8702$ Å, $r_{Au-H} = 1.52385$ Å) in accordance with previous investigations.[59,60] We make the identification of singlet and triplet states based on the intensity of the transition.

We begin by investigating the Group 12 atoms, which have been throughly investigated both experimentally and theoretically. The states that we investigate correspond to *s* to *p* type transitions. Because our RT-TDDFT method can only detect electronically allowed transitions, the only reason we are able to detect the singlet to triplet transitions (the ^{3}P$_1$ states) is because the two-component X2C Hamiltonian includes spin-orbit couplings which allow the otherwise spin-forbidden transitions to become weakly allowed. The spectra are given in Fig. 1. For Zn (and to some extent Cd), the spin-forbidden transition appears almost non-existent. Despite this, the two-component X2C RT-TDDFT method can still observe a slight optical transition, which is observed experimentally. By the time we get to Hg, the singlet to triplet transition is relatively bright. A comparison of our results with both four-component RT-TDDFT and four- and two-component LR-TDDFT is given in Tab. 1. In general we find excellent agreement with both four- and two-component methods for RT-TDDFT and LR-TDDFT, as well as the experimental values obtained from Ref 59. The relatively slight differences between methods likely corresponds to differences in the choice of basis set.

Finally, we compare our results for two diatomic heavy-element hydrides, TlH and AuH. These too have been the subject of much experimental and theoretical studies. Plots of the computed absorption spectrum are given in Figs. 2 and 3 and comparison of selected low energy states with existing theoretical methods are given in Tab. 2. For TlH, we examine the two lowest states, corresponding to $^3\Pi$ and $^1\Pi$ states. Our results for TlH agree very closely with the two-component ZORA with Slater-type functions obtained by Wang, *et al.*. We observe a non-zero transition moment to the $^3\Pi$ state, which is possible only because our two-component X2C Hamiltonian contains spin-orbit interactions to allow this otherwise spin-forbidden transition. We observe a similar behavior with AuH, and our results are only a few hundredths of an eV different from both four- and two- component results. We also note that our results, along with the other literature results, agree strongly with the experimental data, taken from Ref. 60.

4 Conclusion

Here we have implemented a real-time propagation method for solving the relativistic two-component time-dependent X2C equations within the context of density functional theory. We have compared our results for a variety of simple benchmark systems that have been thoroughly investigated by four- and two-component relativistic methods based on both real-time and linear response approaches. Our results show very good agreement with previous studies. We show that the accuracy of our method is comparable to the full four-component relativistic equations, yet with reduced cost because we work within the two-component space. This is the clearest advantage over the previously reported real-time four-component TDDFT method. Because the real time approach is fundamentally non-perturbative, this method is easily extended to study non-linear responses and molecules in strong fields, which is not possible within the linear response formalism. Additionally, because the two component X2C includes spin-orbit operators, this method will be suitable for the description of otherwise spin-forbidden transitions as well as for the description of spin-orbit corrections to high energy excited states, such as those found in X-ray spectroscopy.

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Table 1. Calculated $ns^2 \rightarrow ns^1np^1$ Excitation Energies of Group 12 Atoms ($n = 4-6$ for Zn, Cd, Hg)

		Excitation Energy (eV)							
		RT-TDDFT		LR-TDDFT					
atom	state	this work	Repisky[41]	Gao[26]/Li[37]	Bast[27]	Wang[28]	Nakata[30]	Kühn[29]	exp[59]
Zn	$^1P_1$	5.90	5.84	6.07/5.77	5.76	5.76	6.20	—	5.80
	$^3P_1$	4.30	4.30	4.40/4.35	4.35	4.35	4.41	—	4.03
Cd	$^1P_1$	5.31	5.44	5.50/5.47	5.34	5.35	5.74	5.47	5.42
	$^3P_1$	3.82	4.02	4.04/4.03	4.02	4.02	4.11	4.12	3.80
Hg	$^1P_1$	6.99	6.56	6.66/6.54	6.53	6.53	6.85	6.57	6.70
	$^3P_1$	5.24	5.06	5.12/5.10	5.08	5.09	5.26	5.12	4.89

Table 2. Vertical Excitation Energies of Low-Lying Electronic States of TlH and AuH

		Excitation Energy (eV)					
		RT-TDDFT		LR-TDDFT			
molecule	state	this work	Repisky[41]	Wang[28]	Gao[26]	Kühn[29]	exp[60]
TlH	$^3\Pi$	2.10	2.07	2.08	—	2.09	2.20
	$^1\Pi$	2.88	2.96	2.88	—	2.64	3.00
AuH	$^1\Sigma^+$	3.48	3.31	3.42	3.39	—	3.43
	$^3\Pi$	4.65	4.52	4.70	4.66	—	4.78
	$^1\Pi$	4.98	5.21	5.01	4.96	—	5.32

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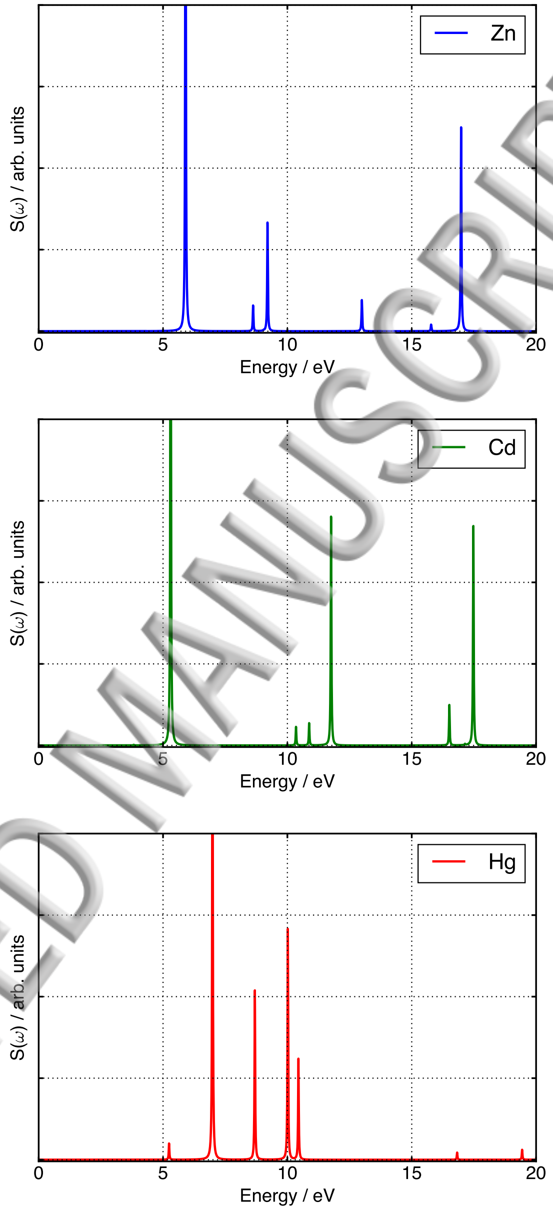


Figure 1. Computed optical absorption spectra of (a) Zn, (b) Cd, and (c) Hg using RT-X2C-TDDFT within the SVWN5/Sapporo-DKH3-2012 level of theory with diffuse-*sp* functions.

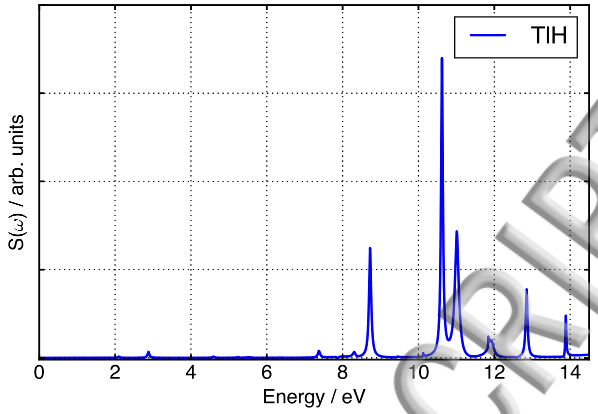


Figure 2. Computed optical absorption spectra of TlH using RT-X2C-TDDFT within the SVWN5/Sapporo-DKH3-2012 level of theory with diffuse-*sp* functions. The TlH bond length corresponds to an experimental equilibrium length of 1.8702 Å.

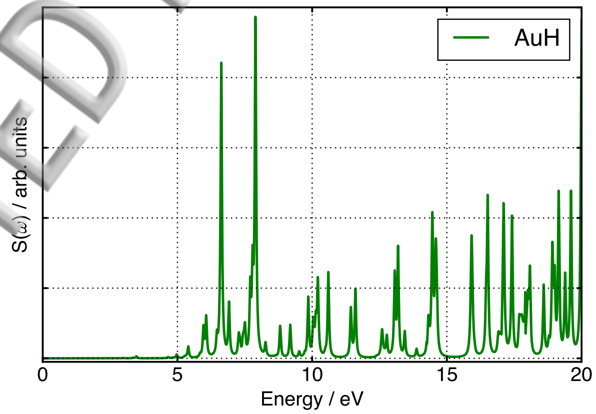
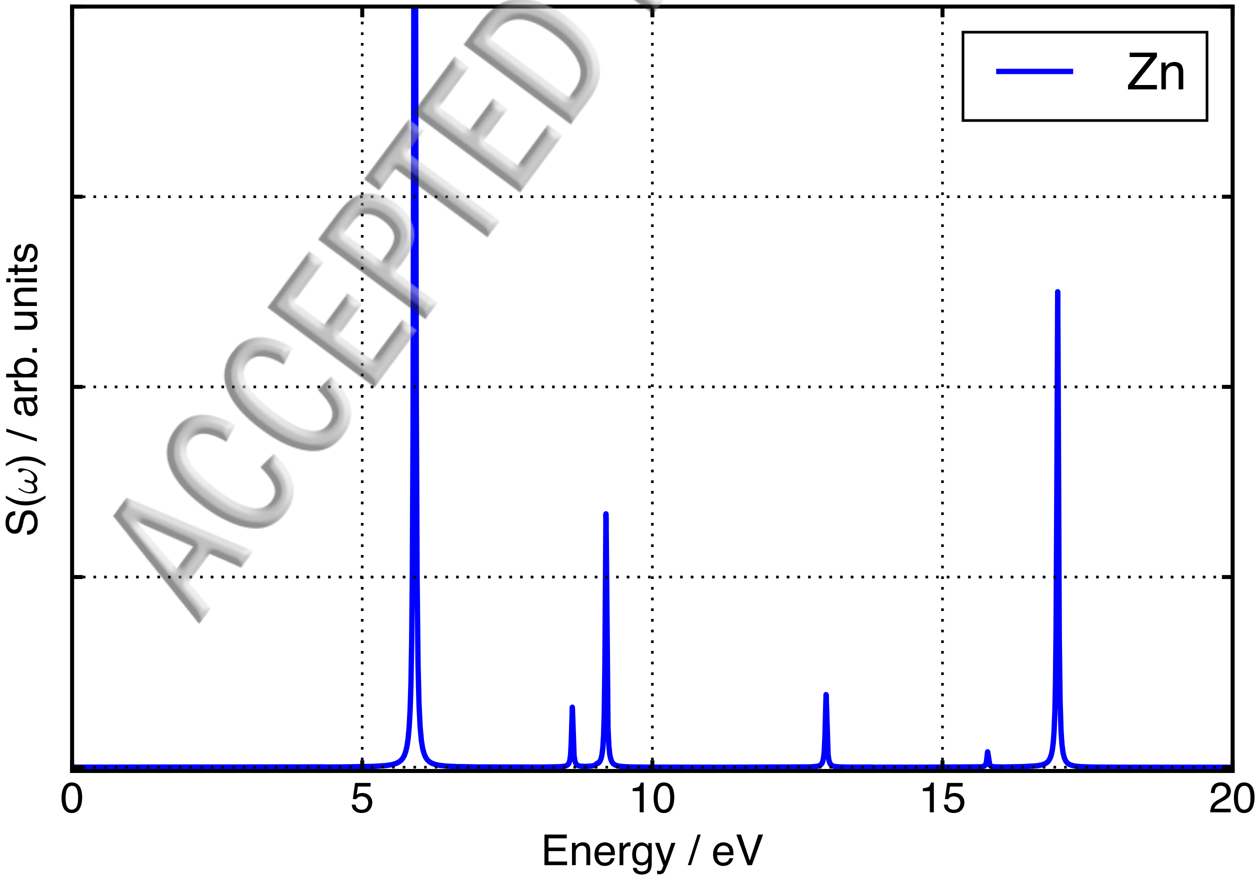


Figure 3. Computed optical absorption spectra of AuH using RT-X2C-TDDFT within the SVWN5/Sapporo-DKH3-2012 level of theory with diffuse-*sp* functions. The AuH bond length corresponds to an experimental equilibrium length of 1.52385 Å.


Zn
S(ω) / arb. units
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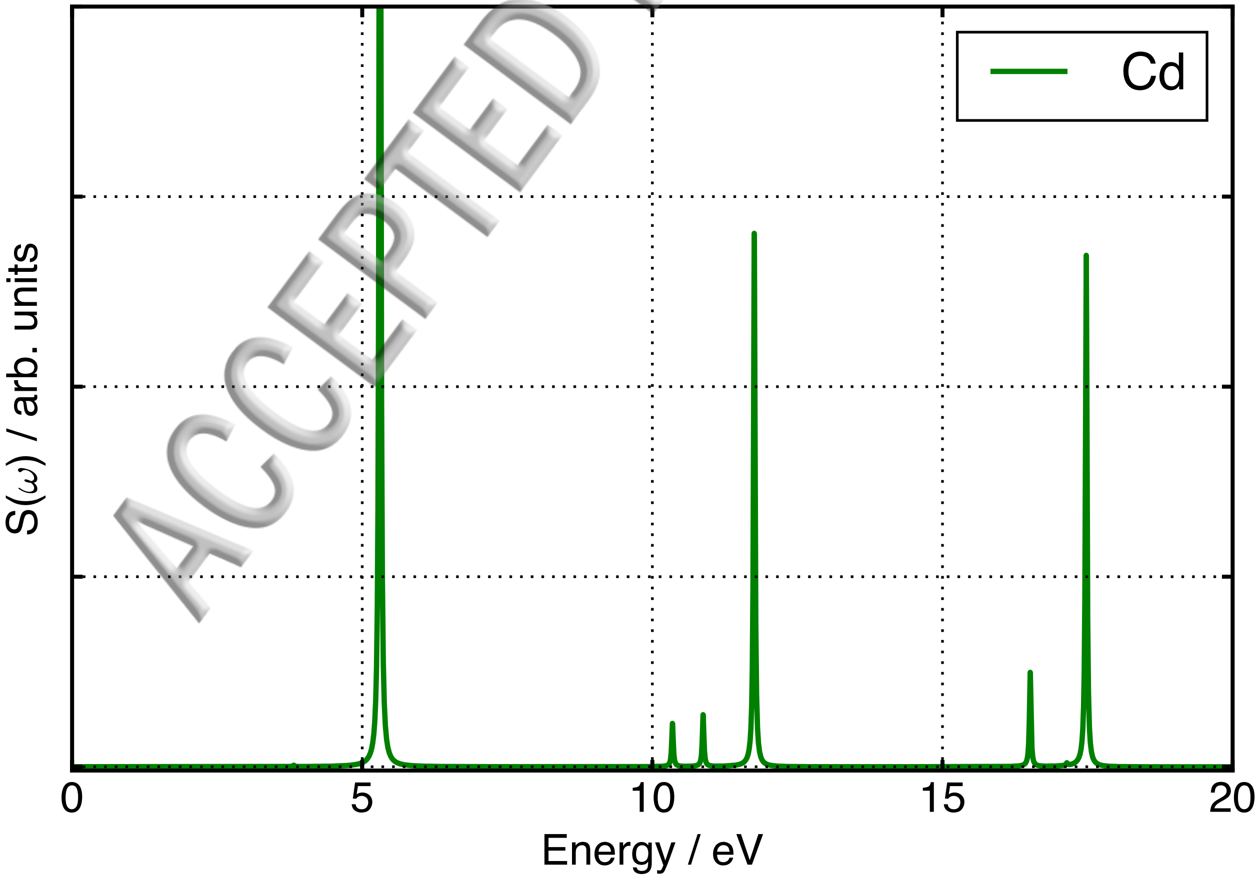
5
10
15
20
Energy / eV


S(ω) / arb. units
Energy / eV
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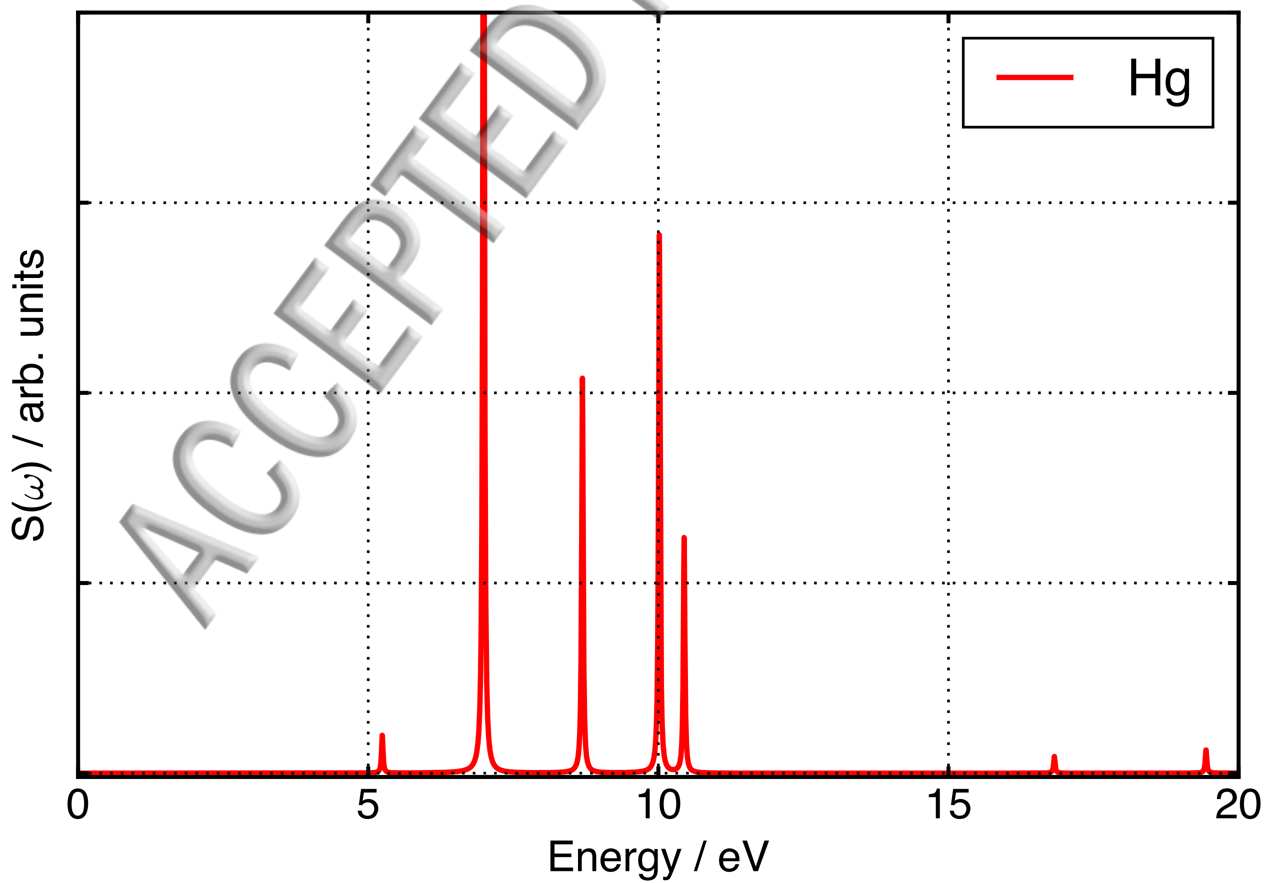
5
10
15
20
Cd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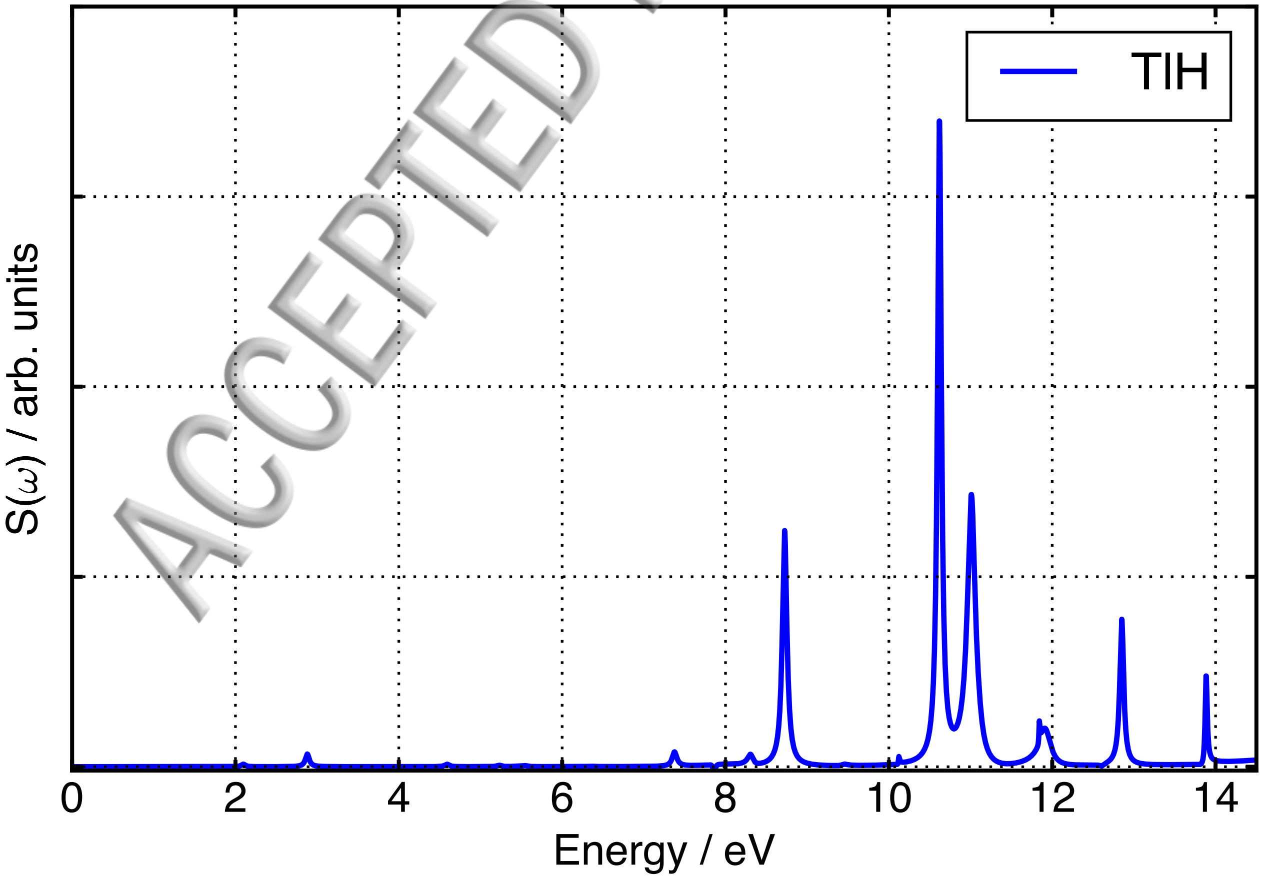
10
15
20
Energy / eV


TlH
S(ω) / arb. units
Energy / eV
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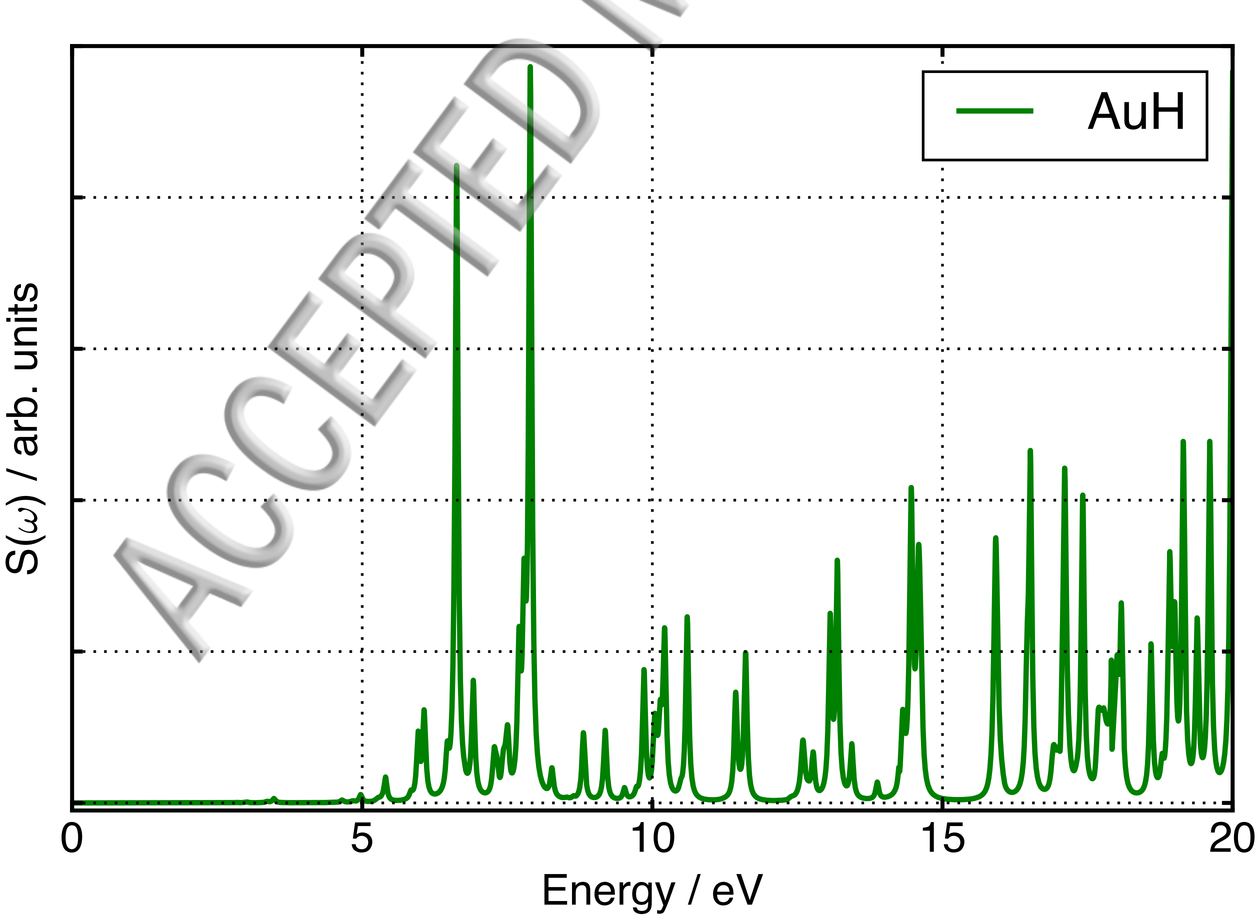
2
4
6
8
10
12
14


AuH
S(ω) / arb. units
Energy / eV
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10
15
20