

Supporting Information

A generalized variational principle with applications to excited state mean field theory

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S.1 Line search details

In scenarios where the current variable is far from a stationary point (i.e. violates the second order Taylor expansion used in the FDNR approximation) or there was an incomplete convergence of the GMRES solver, the convergence of the FDNR algorithm is accelerated by including a parameter ξ that scales the change to the variable vector according to

$$\vec{v}_{k+1} = \vec{v}_k + \xi \Delta \vec{v}_k. \quad (1)$$

The update vector $\Delta \vec{v}_k$ is the optimal direction we should move in, yet the overall optimization may converge faster if we can determine algorithmically how far we should move that direction in parameter space. The line search algorithm described in this section and illustrated in Figure 1 identifies the step size, reducing the impact of “bad steps” and maximizing the effect of “good steps” towards the desired energy stationary point.

After computing the descent direction $\Delta \vec{v}_k$ via the GMRES algorithm, we then aim to minimize $g(\xi) = f(\vec{v}_k + \xi \Delta \vec{v}_k)$, where f is a target function for the line search. This target function need not be identical to the main algorithm’s target function like $L_{\vec{\lambda}}$ or $L_{\mu\chi}$; in fact, we most often used the energy as the line search target function as it is cheaper to compute than other potential line search target function candidates such as L , $|\nabla E|$, or $|\nabla L|$. However, minimizing the energy is not ideal in scenarios where $\Delta \vec{v}_k$ mainly affects energy-invariant parameters such as the lagrange multipliers in $L_{\vec{\lambda}}$. For cases where the line search seemed inefficient or failed when minimizing the energy, we

instead used L as the line search target function.

Once we have selected a target function, we then identify two points with opposite-signed derivatives, ξ_L and ξ_R . Although we use the approximate derivative

$$D(\xi) \approx \frac{g(\xi + \delta) - g(\xi)}{\delta} \quad (2)$$

as another cost saving measure, by the intermediate value theorem, we are guaranteed that ξ_L and ξ_R are left- and right-side bounds, respectively, for the line search step size that minimizes $g(\xi)$, ξ_0 .

With these new bounds, we then start with a bisection search, where a central point is suggested according to $\xi_C = \frac{1}{2}(\xi_L + \xi_R)$. If $D(\xi_L) < D(\xi_C) < 0$, the central point becomes the new left-side bound, i.e. $\xi_C \rightarrow \xi_L$. Alternatively, if $0 < D(\xi_C) < D(\xi_R)$, $\xi_C \rightarrow \xi_R$. This first bisection search tightens the bounds closer to the minimum. Then, the line search generates a few points between the bounds and attempts to fit the function $g(\xi)$ with the two or three points with smallest values of $D(\xi)$ to either a linear or quadratic polynomial to produce an estimate to ξ_0 . If this new estimate does not have a sufficiently small value of $D(\xi_0)$, the line search reverts back to a bisection search. Overall, the linesearch is quite robust, computationally cheap – converging in about twenty function calls, and greatly improves the speed and numerical stability of the FDNR algorithm.

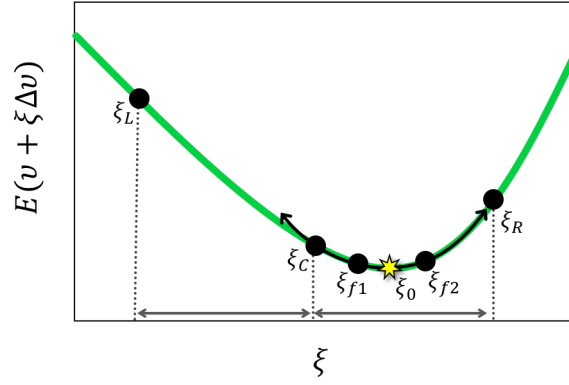


Figure 1: A fictitious example illustrating the line search is shown. The energy of the wave function is the target function and is plotted against ξ in green. The initial bounds are chosen such that the target function is decreasing at ξ_L and increasing at ξ_R . An initial bisection search locates ξ_C , the central point between the bounds as shown by the dashed lines and double-headed gray arrows, and this point becomes the new left-most bound to the minimum. Two more points are generated between the bounds, ξ_{f1} and ξ_{f2} , and a parabola – plotted in black – is fit to those three points with smallest values of $D(\xi)$: ξ_C , ξ_{f1} , and ξ_{f2} . The minimum of that parabola shown by the yellow star is approximately ξ_0 – the value that minimizes $E(v + \xi \Delta v)$.

S.2 Excitation Energies Results

Table 1: CSF coefficients in the ESMF wave function with amplitudes larger than 0.1 are tabulated for each molecule in the test set. Orbital ordering is relative to RHF orbital energies produced by MOLPRO version 2019.1. Note that other levels of theory may have different orbital energies, and thus orbital orderings. In these scenarios, we ensured we were comparing the same excitations by plotting and visually comparing orbitals contributing to the major CSFs in the excitations between theories.

Molecule	Excitation	CSF Amplitude
Acetaldehyde	HOMO → LUMO	0.65
	HOMO-5 → LUMO	0.17
	HOMO-4 → LUMO	-0.15
Ammonia	HOMO → LUMO	0.70
Carbon Monoxide	HOMO → LUMO	0.70
Cyclopropene	HOMO → LUMO	0.68
	HOMO → LUMO+3	-0.19
Diazomethane	HOMO → LUMO	0.68
	HOMO → LUMO+3	-0.16
Dinitrogen	HOMO-1 → LUMO	0.49
	HOMO → LUMO+1	0.49
Ethylene	HOMO → LUMO	0.69
Formaldehyde	HOMO → LUMO	0.66
	HOMO-3 → LUMO	0.22
Formamide	HOMO-1 → LUMO+2	0.68
	HOMO-4 → LUMO+2	-0.11
Hydrogen Sulfide	HOMO → LUMO	0.70
Ketene	HOMO → LUMO	0.69
	HOMO → LUMO+3	0.14
Methanimine	HOMO → LUMO	0.67
	HOMO-2 → LUMO	-0.17
Nitrosomethane	HOMO → LUMO	0.65
	HOMO-5 → LUMO	0.21
	HOMO-2 → LUMO	0.14
Streptocyanine Cation	HOMO → LUMO	0.70
Thioformaldehyde	HOMO → LUMO	0.70
Water	HOMO → LUMO	0.70
Ammonia → Difluorine	HOMO → LUMO	0.70
Dinitrogen → Methylene	HOMO-3 → LUMO	0.70

Table 2: Comparisons for singlet excitations from the ground state in the cc-pVDZ basis set. We report δ -CR-EOM-CC(2,3),D excitation energies in eV, with other methods’ results reported as excitation energy errors in eV relative to δ -CR-EOM-CC(2,3),D and summarized in terms of mean unsigned error (UE) and maximum UE.

Molecule	δ -CR-EOM-CC(2,3),D (eV)	CIS	CIS(D)	EOM-CCSD	TD-DFT B3LYP	TD-DFT ω B97X-V	ESMF	ESMP2
Acetaldehyde	4.36	0.71	0.25	0.21	0.09	0.14	-0.63	0.15
Ammonia	7.57	0.95	0.06	0.05	-0.52	-0.07	-0.46	-0.01
Carbon Monoxide	8.76	0.61	0.51	0.30	0.16	0.31	0.05	-0.16
Cyclopropene	7.97	0.57	-0.33	-0.08	-0.83	-0.33	-0.41	-0.06
Diazomethane	3.01	0.38	0.82	0.45	0.05	0.09	-0.67	-0.04
Dinitrogen	10.36	-1.31	0.62	0.44	-0.03	0.00	-1.39	0.06
Ethylene	8.80	-0.25	0.12	0.19	0.11	0.10	-0.43	-0.29
Formaldehyde	4.08	0.63	0.25	0.19	0.07	0.10	-0.69	0.15
Formamide	5.86	0.88	0.16	0.21	0.04	0.11	-0.79	0.13
Hydrogen Sulfide	7.05	0.58	0.24	0.11	-0.27	0.20	0.00	-0.07
Ketene	3.78	0.70	0.59	0.36	0.22	0.31	-0.23	-0.05
Methanimine	5.35	0.66	0.35	0.22	0.00	0.11	-0.59	-0.02
Nitrosomethane	1.85	0.27	0.30	0.25	0.13	0.12	-0.41	0.17
Streptocyanine Cation	7.53	1.55	0.07	0.28	1.08	1.07	0.21	-0.42
Thioformaldehyde	2.18	0.58	0.26	0.24	0.13	0.17	-0.54	-0.08
Water	8.30	1.02	-0.12	-0.01	-0.57	-0.22	-0.67	0.05
Ammonia $\rightarrow$ Difluorine	9.27	2.38	-0.78	0.51	-6.91	-2.69	-1.49	-0.27
Dinitrogen $\rightarrow$ Methylene	15.49	1.66	0.26	0.60	-6.58	-1.79	-0.69	0.15
Max UE		2.38	0.82	0.60	6.91	2.69	1.49	0.42
Mean UE		0.87	0.34	0.26	0.99	0.44	0.58	0.13

S.3 Molecular Geometries

All geometries are reported in Bohr.

Acetaldehyde

C	0.008052747	0.000000000	0.879198997
C	-1.761806316	0.000000000	-1.344481077
O	2.246773638	0.000000000	0.718590585
H	-0.904428111	0.000000000	2.736770916
H	-2.977891958	1.652861299	-1.265947535
H	-2.977891958	-1.652861299	-1.265947535
H	-0.702745912	0.000000000	-3.092549493

Ammonia

N	0.111541492	0.000000002	0.000000000
H	-0.587537797	0.880428810	-1.524947426
H	-0.587537798	-1.760857612	0.000000000
H	-0.587537797	0.880428810	1.524947426

Carbon Monoxide

C	0.000000000	0.000000000	-1.230609558
O	0.000000000	0.000000000	0.873855928

Cyclopropene

C	0.000000000	0.000000000	-0.872109716
C	0.000000000	0.638080734	0.479769238
C	0.000000000	-0.638080734	0.479769238
H	0.902756928	0.000000000	-1.470452899
H	-0.902756928	0.000000000	-1.470452899
H	0.000000000	1.563989148	1.011157668
H	0.000000000	-1.563989148	1.011157668

Diazomethane

C	0.000000000	-0.000000000	-2.282953315
N	0.000000000	0.000000000	0.137388906
N	0.000000000	-0.000000000	2.246110349
H	0.000000000	1.784627456	-3.225240635
H	0.000000000	-1.784627456	-3.225240635

Dinitrogen

N	0.000000000	0.000000000	1.018666600
N	0.000000000	0.000000000	-1.018666600

Ethylene

C	0.000000000	1.244689439	0.000000000
C	0.000000000	-1.244689439	0.000000000
H	0.000000000	2.315999946	1.727974166
H	0.000000000	-2.315999946	1.727974166
H	0.000000000	2.315999946	-1.727974166
H	0.000000000	-2.315999946	-1.727974166

Formaldehyde

C	0.000000000	0.000000000	-1.126692899
O	0.000000000	0.000000000	1.111413933
H	0.000000000	1.746571764	-2.224070962
H	0.000000000	-1.746571764	-2.224070962

Formamide

C	-0.759239486	0.000000000	0.680863915
O	1.465517414	0.000000000	0.317888436
N	-2.536583216	0.000000000	-1.145481407
H	-1.567254484	0.000000000	2.576881356
H	-2.001519756	0.000000000	-2.949041662
H	-4.368936239	0.000000000	-0.742367881

Hydrogen Sulfide

S	0.000000000	0.000000000	-0.468754348
H	0.000000000	1.838805844	1.234674624
H	0.000000000	-1.838805844	1.234674624

Ketene

C	0.000000000	0.000000000	-2.433659698
C	0.000000000	0.000000000	0.034004982
O	0.000000000	0.000000000	2.198008243
H	0.000000000	1.764688153	-3.424475103
H	0.000000000	-1.764688153	-3.424475103

Methanimine

C	0.103417399	0.000000000	1.094801643
N	0.091622833	0.000000000	-1.268355130
H	-1.575250900	0.000000000	2.268386439
H	1.888324157	0.000000000	2.082404864
H	-1.679726679	0.000000000	-1.958372417

Nitrosomethane

C	-1.769950191	0.000000076	-1.063258407
N	0.005900793	-0.000000079	1.056243005
O	2.140923687	-0.000000375	0.438685065
H	-0.784206011	-0.000000174	-2.854317255
H	-2.958034437	1.656486501	-0.863557788
H	-2.958034952	-1.656485950	-0.863557601

Streptocyanine Cation

C	0.000000000	0.000000000	0.799430664
N	0.000000000	2.179904146	-0.330459605
N	0.000000000	-2.179904146	-0.330459605
H	0.000000000	0.000000000	2.828681969
H	0.000000000	2.361047263	-2.212325178
H	0.000000000	-2.361047263	-2.212325178
H	0.000000000	3.775585653	0.677824117
H	0.000000000	-3.775585653	0.677824117

Thioformaldehyde

C	0.000000000	0.000000000	-2.074807692
S	0.000000000	0.000000000	0.943242493
H	0.000000000	1.723389730	-3.161483020
H	0.000000000	-1.723389730	-3.161483020

Water

O	0.000000000	0.000000000	-0.112851412
H	0.000000000	1.425999575	0.970077421
H	0.000000000	-1.425999575	0.970077421

Ammonia → Fluorine

N	0.000000000	-0.443921233	-6.652831844
H	0.000000000	1.331763699	-7.379272802
H	1.537789200	-1.331763699	-7.379272802
H	-1.537789200	-1.331763699	-7.379272802
F	0.000000000	-0.443921233	4.685524903
F	0.000000000	-0.443921233	7.379272802

Dinitrogen → Methylene

C	0.000000000	0.000000000	-10.173779784
N	0.000000000	0.000000000	9.530551979
N	0.000000000	0.000000000	11.567891822
H	0.000000000	1.623731296	-11.462151350
H	0.000000000	-1.623731296	-11.462151350

Lithium Hydride (Stretched)

Li	0.000000000	0.000000000	0.000000000
H	0.000000000	0.000000000	13.228082872