The Journal of Chemical Physics

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Cite as: J. Chem. Phys. **150**, 214103 (2019); https://doi.org/10.1063/1.5090983
Submitted: 31 January 2019 . Accepted: 08 May 2019 . Published Online: 03 June 2019

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The Journal of Chemical Physics ARTICLE scitation.org/journal/jcp

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Submitted: 31 January 2019 • Accepted: 8 May 2019 •
Published Online: 3 June 2019

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ABSTRACT

We present an energy-dependent explicitly correlated (F12) formalism for the nondiagonal renormalized second-order (NR2) Green's function method of closed-shell molecules. For a test set of 21 small molecules, the mean basis set error in IP computed using NR2-F12 with aug-cc-pVTZ basis is 0.028 eV, compared to 0.044 eV for NR2 with aug-cc-pV5Z basis. Similarly, for a set of 24 medium-sized organic electron acceptor molecules (OAM24), the mean basis set errors are 0.015 eV for NR2-F12 with aug-cc-pVTZ basis compared to 0.067 eV for NR2 with aug-cc-pVQZ basis. Hence, NR2-F12 facilitates accurate calculation of IP at a lower cost compared to the NR2 method. NR2-F12 has $\mathcal{O}(N^6)/\mathcal{O}(N^5)$ *noniterative*/*iterative* costs with system size. At a small basis, the performance of NR2-F12 for 21 small molecules and OAM24 dataset is comparable to equation-of-motion ionized coupled-cluster singles and doubles, whose cost is *iterative* $\mathcal{O}(N^6)$.

I. INTRODUCTION

Green's function (GF) (propagator) formalisms are the foundation of the many-body electronic structure in physics.[1–3] This is also the case in chemistry,[4–6] where they draw increasing attention as an alternative to wave function/operator methods[7–13] as well as a way to systematically improve the density functional theory.[14–18] Although the recent chemistry literature has utilized single-particle and polarization propagators for computing total correlation energies[19,20] and as a basis for quantum mechanical embedding methods,[21–24] the traditional application of single-particle (electron) propagator (EP) methods were for computing ionization potential (IP), electron affinity (EA), and photoelectron spectra.[25–33] The appeal of propagator methods is their direct connection to the observables as well as their interpretive power.[34]

Conventional spectral solvers for propagator methods, utilizing expansions in a Fock subspace built from a finite single-particle basis, suffer from slow asymptotic decay of basis set errors of energies (such as ionization potentials and total correlation energies) and other properties. This is due to the inability to model efficiently localized features such as electron-electron cusps with products of single-particle basis functions. Explicitly correlated wave function methods solve this problem by introducing 2-particle basis functions that describe the cusp structure directly. The R12/F12 wave function methods realized this idea practically by approximating the many-electron integrals by resolution of the identity and other techniques following the original ideas by Kutzelnigg[35] and finalized by many others.[36–44] Recently, the explicitly correlated F12 formalism was also applied to propagator methods. Ohnishi and Ten-no utilized MP2-F12 energies to correct the *diagonal* elements of self-energy at *unperturbed* (Koopmans) energies;[45] recently this approach was reformulated using stochastic integration formalism and applied to large systems.[46] General *nondiagonal energy-dependent* F12 correction to the second-order self-energy (GF2-F12) was proposed by some of us.[47] The GF2-F12 method scales as iterative $\mathcal{O}(N^5)$ and shows much faster convergence to the complete basis set (CBS) limit than the standard GF2 counterpart, thus requiring only a triple-zeta basis to reduce the numerical error in ionization potentials below 0.05 eV. However, the accuracy of the second-order (non-self-consistent) model of self-energy is limited and more complete models of self-energy must be utilized.

Among nondiagonal EP methods,[34,48] the nondiagonal renormalized second-order (NR2) approximation of EP is a promising method to calculate ionization potentials.[49] Numerical results indicate that the performance of NR2 is the best among nondiagonal EP methods at a complete basis set limit.[50] In this article, we investigate the basis set convergence of an energy dependent F12 correction to the NR2 method. IPs calculated with NR2-F12 for small and medium sized organic molecules (Fig. 1) are compared to GF2-F12, equation-of-motion ionized coupled-cluster singles and doubles (EOM-IP-CCSD), coupled-cluster with perturbative triples (CCSD(T)) reference IPs extrapolated to CBS limit and perturbative inclusion of explicitly correlated terms (CCSD(T)-F12).

This article is organized as follows. Section II introduces the NR2 method and how its basis set error is reduced via an F12 correction to self-energy. The implementation details are included in Sec. III. Basis set errors of NR2-F12, their accuracy compared to other methods against a CCSD(T) benchmark, are presented in Sec. IV, followed by conclusions in Sec. V.

II. FORMALISM

We have used the time-independent (superoperator) EP formalism in this work.[6,52] The eigenvalues, which correspond to the poles of EP are obtained by solving the Dyson quasiparticle equation self-consistently. The Dyson equation is an eigenvalue problem given by

$$[\mathbf{F} + \mathbf{\Sigma}(E)]\mathbf{C} = E\mathbf{C}. \tag{1}$$

In this equation, $\mathbf{\Sigma}(E)$ is the energy-dependent nonlocal potential called the self-energy; $\mathbf{F}$ is the Fock matrix and $\mathbf{C}$ are canonical Hartree-Fock orbitals in case of a diagonal self-energy and Dyson orbitals for a nondiagonal self-energy. The off-diagonal elements of the self-energy matrix in canonical basis are small and have negligible effect on the poles and the Dyson orbitals. The derivation and approximations to the Dyson quasiparticle equation are discussed by Corzo and Ortiz.[48]

The focus of this work is on a particular model for the self-energy operator—specifically, the Nondiagonal Renormalized 2nd-order (NR2) model—proposed by Ortiz.[49] Recently it has been demonstrated as a particularly cost-effective way to compute accurate ionization potentials and electron affinities of lowest IP/EA of organic molecules.[50] The non-Hermitized NR2 self-energy for electron detachment (NR2-D) is represented as follows:

$$\begin{aligned}
\mathbf{\Sigma}_{ij}(E) &= (a_i|\hat{H}a^c_{kl})^{(1)}(a^c_{kl}|(E\hat{1}-\hat{H})^{-1}a^d_{mn})^{(1)}(a^d_{mn}|\hat{H}a_j)^{(2)} \\
&\quad + (a_i|\hat{H}a^k_{cd})^{(1)}(a^k_{cd}|(E\hat{1}-\hat{H})^{-1}a^l_{ef})^{(0)}(a^l_{ef}|\hat{H}a_j)^{(1)}, \\
\mathbf{\Sigma}_{ai}(E) &= (a_a|\hat{H}a^c_{kl})^{(1)}(a^c_{kl}|(E\hat{1}-\hat{H})^{-1}a^d_{mn})^{(1)}(a^d_{mn}|\hat{H}a_i)^{(2)} \\
&\quad + (a_a|\hat{H}a^k_{cd})^{(1)}(a^k_{cd}|(E\hat{1}-\hat{H})^{-1}a^l_{ef})^{(0)}(a^l_{ef}|\hat{H}a_i)^{(1)}, \\
\mathbf{\Sigma}_{ia}(E) &= [\mathbf{\Sigma}_{ai}(E)]^*, \\
\mathbf{\Sigma}_{ab}(E) &= (a_a|\hat{H}a^c_{kl})^{(1)}(a^c_{kl}|(E\hat{1}-\hat{H})^{-1}a^d_{mn})^{(0)}(a^d_{mn}|\hat{H}a_b)^{(1)} \\
&\quad + (a_a|\hat{H}a^k_{cd})^{(1)}(a^k_{cd}|(E\hat{1}-\hat{H})^{-1}a^l_{ef})^{(0)}(a^l_{ef}|\hat{H}a_b)^{(1)},
\end{aligned} \tag{2}$$

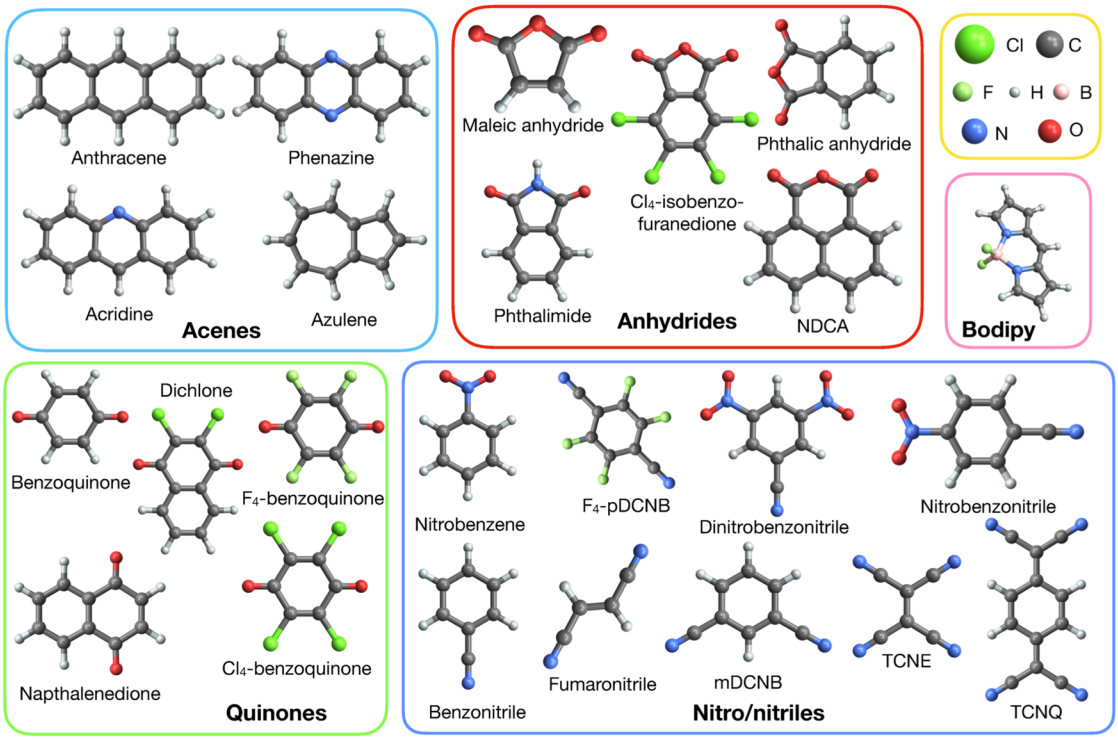

FIG. 1. Benchmark set of 24 medium sized organic molecules (OAM24) from Ref. 51 used in this work.

where the matrix elements of the superoperator are defined as

$$(\mu|\nu) = \langle 0|[\mu^\dagger, \nu]_+(1 + \hat{T}_2^{(1)})|0\rangle, \tag{3}$$

where $|0\rangle$ is the Hartree-Fock reference state and $\hat{T}_2^{(1)}|0\rangle$ is the first-order Møller-Plesset (MP) wave function. We have used standard Einstein-summed tensor notation for products of annihilation (a_p) and creation ($a^p \equiv a_p^\dagger$) operators that are normal ordered with respect to the physical vacuum.[53] Indices $i, j, \ldots$ refer to the active occupied orbitals (holes), $a, b, \ldots$—to the unoccupied (particle) orbitals represented in the orbital basis set (OBS), p, q, r—to any (hole or particle) active orbital represented in OBS, and α, β—to the unoccupied orbitals of the complete basis set (CBS). The superscript indices on superoperator matrix elements denote the *maximum* order (in the MP sense) of the terms kept, and the operator inverse is defined by the inverse of its given basis representation. The Hermitized expressions for NR2-D were used in practice and are given by Corzo and Ortiz.[48]

The high accuracy of NR2 IPs/EAs is only revealed when the numerical error is eliminated. Unfortunately, the rate of basis set convergence of IPs/EAs is slow due to the slow convergence of summations over unoccupied states in the (to leading order) $2p1h$ component of the self-energy. This is illustrated for the lowest-energy detachment pole of the energy-dependent diagonal second-order self-energy in Fig. 2. It is easy to see that the basis set convergence of the $2h1p$ and $2p1h$ components [the first and second terms on the right-hand side of Eq. (2)] of the self-energy are fundamentally different. In an atom, exact evaluation of the $2h1p$ contribution only requires the basis of 1-particle states to be complete through $3L_{\rm occ}$, where $L_{\rm occ}$ is the maximum angular momentum of an occupied orbital (this roughly explains why for p-elements the $2h1p$ contribution is essentially converged with a TZ basis, which is first to gain basis functions of angular momentum 3). In contrast, the summation over the particle states in the $2p1h$ term does not truncate and thus is analogous to the slowly convergent error of truncated partial wave expansion of the atomic correlation energies.[54] To reduce the basis set error of this term, some kind of basis set extrapolation is typically employed. However, a more robust solution to the basis set problem is to employ explicit correlation.

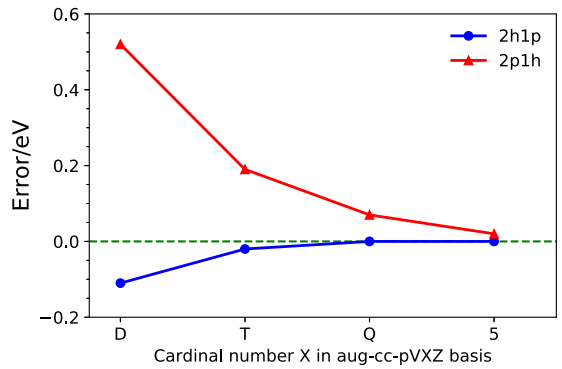

FIG. 2. Basis set errors in $2h1p$ and $2p1h$ contributions to first ionization potential of aN_2 molecule evaluated with the noniterative diagonal second-order self-energy model.

The explicitly correlated R12/F12 formalism[35,41–43] has been established as the standard solution to the basis set problem of wave function methods in which the many-electron basis includes terms with explicit dependence on the inter-electronic distances. Such formalism can be also extended to the self-energy operator as we recently showed in the case of (nondiagonal) energy-dependent case;[47] note that our approach specifically accounts for the energy dependence of the explicitly correlated term. The energy-dependent F12 correction to self-energy is obtained by augmenting the slowly convergent $\mathbf{f} = \{a_{ab}^i\}$ operator manifold with the geminal field operator manifold, $\mathbf{f}^\gamma$, given by

$$\mathbf{f}^\gamma = \frac{1}{2}\tilde{R}_{ir}^{\alpha\beta}\tilde{a}_{\alpha\beta}^i, \tag{4}$$

where $\tilde{R}$ is the antisymmetrized matrix element of the geminal correlation factor $f(r_{12})$ given by

$$R_{ir}^{\alpha\beta} \equiv \langle ir|\hat{Q}f(r_{12})|\alpha\beta\rangle, \tag{5}$$

and the projector $\hat{Q}$ ensures orthogonality of geminal and conventional $2h1p$ field operators. By neglecting the coupling blocks of the superoperator between the conventional and F12 manifolds, the conventional $2p1h$ self-energy is corrected by *addition* of the F12 contribution

$$\mathbf{\Sigma}_{\rm F12}(E) = (\mathbf{a}|\hat{H}^{(1)}\mathbf{f}^\gamma)(\mathbf{f}^\gamma|(E - \hat{H}^{(0)})\mathbf{f}^\gamma)^{-1}(\mathbf{f}^\gamma|\hat{H}^{(1)}\mathbf{a}). \tag{6}$$

Since the conventional $2p1h$ contribution to the self-energy in the NR2-D approach is identical to its GF2 counterpart, we obtain the NR2-F12 self-energy expression for the detachment processes by simple addition of the F12 self-energy correction; note that for the NR2-A approach, we expect that the F12 correction will need to be modified to account for the presence of the higher-order terms in the $2p1h$ self-energy. The $2h1p$ contribution to the NR2 or GF2 self-energy is not affected by the F12 terms, and it converges quickly to the CBS limit.

The structure of the coupling between the conventional and F12 manifolds in the GF2-F12 and NR2-D-F12 methods is completely analogous to their coupling in the MP2-F12 method (e.g., see Refs. 55 and 41); namely, it involved matrix elements of the Fock operator between the conventional unoccupied orbitals and their complement in the complete basis. The effect of the coupling on the MP2-F12 energies is smaller than the residual basis set errors (and the method errors) and becomes completely negligible with triple-zeta and larger basis sets,[55] and for the ionization potentials, we expect the same trends. Since the 2h1p channel's contribution to the self-energy requires a triple-zeta basis anyway, the neglect of the coupling is justified.

Resolution of matrix elements of Eq. (6) yields standard F12 intermediates V, X, and B.[47] The derivation and programmable equations of these terms are available in the literature.[41] In this work, the intermediates V and X are calculated using the complementary auxiliary basis set (CABS) approach.[56] The bottleneck of evaluating the F12 correction is the intermediate B, which in this work for efficiency was computed in approximation D,[57] rather than the more complete approximation C.[58]

With canonical Hartree-Fock orbital energy as an initial guess, the eigenvalue problem of Eq. (1) is solved iteratively until the root is converged with the energy-dependent F12 correction to self-energy included in every iteration.

TABLE I. Mean absolute (MAE) and max absolute (MaxAE) basis set errors in eV of NR2 IPs for the O21 set.

	MAE		MaxAE	
Basis set	NR2	NR2-F12	NR2	NR2-F12
aDZ	0.416	0.049	0.515[a]	0.085[b]
aTZ	0.185	0.028	0.246[c]	0.047[c]
aQZ	0.087	0.015	0.119[c]	0.037[c]
a5Z	0.044		0.061[c]	

[a] CH_3COCH_3.
[b] H_2CO.
[c] HF.

III. COMPUTATIONAL DETAILS

Distributed-memory parallel implementations of NR2 and NR2-F12 methods were developed in the Massively Parallel Quantum Chemistry (MPQC) package.[59] The performance of the NR2-F12 method was assessed for a set of 21 small molecules used previously by Ortiz and co-workers (and referred to here as O21)[60] and the OAM24 benchmark set of 24 medium-sized organic electron acceptor molecules,[51] with the Cartesian geometries taken from the respective references. The frozen core approximation is invoked in all the calculations reported in this work. Standard (global) density fitting (DF) approximation for 2-electron integrals was used for efficiency throughout.

We have used the augmented correlation consistent basis sets that can be reliably extrapolated to the complete basis set (CBS) limit.[61–63] The aug-cc-pVXZ orbital basis (denoted for brevity as aXZ), with X = D,T,Q, and 5, were paired with the corresponding aug-cc-pVXZ-RI basis for density fitting[64] and the aug-cc-pVXZ-OptRI basis for approximating many-electron F12 integrals.[65] The standard Slater-type correlation factor

$$f(r_{12}) = (1 - \exp(-\gamma r_{12})/\gamma) \tag{7}$$

was used in all F12 computations, with the geminal exponent γ set as in Ref. 47 to 1.3, 1.9, and 2.1 a_0^{-1} for the aDZ, aTZ, and aQZ orbital basis sets, respectively. All propagator F12 calculations evaluated intermediate B using approximation D;[57] for the O21 set, the difference in IPs evaluated with the F12/D approach vs the more complete F12/C approach with the aTZ basis was found to be at

TABLE II. Differences of IP in eV of the O21 set calculated using Green's function and coupled-cluster methods with aDZ and aTZ bases relative to CCSD(T) IP extrapolated to the CBS limit.

	GF2-F12		NR2-F12		CCSD(T)-F12		EOM-IP-CCSD			CCSD(T)	
Molecule	aDZ	aTZ	aDZ	aTZ	aDZ	aTZ	aDZ	aTZ	CBS[a]	CBS	Expt.
C_2H_2	−0.018	−0.049	0.177	0.152	−0.063	−0.026	−0.062	0.062	0.149	11.467	11.02
C_2H_4	−0.270	−0.261	−0.075	−0.064	−0.067	−0.025	−0.170	−0.036	0.039	10.713	10.51
C_5NH_5	−0.248	−0.241	−0.012	−0.005	−0.069	−0.029	−0.230	−0.095	−0.017	9.852	9.60
C_6H_6	−0.253	−0.248	0.007	0.022	−0.033	0.011	−0.204	−0.070	0.006	9.421	9.25
$CH_3CH_2CH_3$	−0.306	−0.288	−0.184	−0.162	−0.049	−0.013	−0.189	−0.056	0.014	12.171	11.51
CH_3CHO	−0.988	−0.954	−0.180	−0.135	−0.086	−0.045	−0.347	−0.123	0.012	10.380	10.26
CH_3Cl	−0.280	−0.275	−0.170	−0.207	−0.058	0.021	−0.310	−0.140	0.024	11.495	11.29
CH_3COCH_3	−1.000	−0.966	−0.155	−0.111	−0.081	−0.044	−0.341	−0.111	0.027	9.879	9.70
CH_3F	−0.967	−0.957	−0.265	−0.242	−0.087	−0.039	−0.375	−0.194	−0.059	13.477	13.04
CH_3OH	−0.941	−0.907	−0.199	−0.155	−0.084	−0.049	−0.385	−0.176	−0.044	11.186	10.94
CH_3SH	−0.218	−0.185	−0.185	−0.171	−0.067	0.004	−0.285	−0.083	0.032	9.554	9.46
CH_4	−0.250	−0.240	−0.141	−0.128	−0.060	−0.018	−0.170	−0.042	0.030	14.415	13.60
CO	0.044	0.081	0.078	0.131	0.002	0.002	−0.068	0.123	0.220	14.078	14.01
CO_2	−0.615	−0.606	0.107	0.127	−0.084	−0.071	−0.353	−0.129	0.031	13.906	13.78
H_2CO	−1.051	−1.015	−0.222	−0.173	−0.090	−0.040	−0.388	−0.167	−0.036	11.017	10.88
HCl	−0.201	−0.195	−0.093	−0.135	−0.065	0.031	−0.305	−0.131	0.041	12.845	12.75
HCN	0.037	0.018	0.252	0.245	−0.086	−0.037	−0.051	0.096	0.196	13.734	13.60
HCOOH	−0.988	−0.964	−0.110	−0.074	−0.084	−0.054	−0.341	−0.119	0.028	11.659	11.51
HF	−1.330	−1.345	−0.184	−0.182	−0.018	−0.043	−0.432	−0.247	−0.082	16.295	16.05
N_2	−0.432	−0.406	0.236	0.262	0.011	0.017	−0.187	0.025	0.143	15.579	15.60
H_2S	−0.167	−0.130	−0.151	−0.137	−0.079	0.010	−0.292	−0.079	0.040	10.504	10.48
MAE[b]	0.505	0.492	0.152	0.144	0.063	0.030	0.261	0.110	0.060	0.23[c]	
MaxAE[b]	1.330	1.345	0.265	0.262	0.090	0.071	0.432	0.247	0.220	0.82[c]	

[a] CBS value calculated from X^{-3} extrapolation of {aTZ,aQZ} basis set pair.
[b] Mean and max absolute errors of IP obtained from GF and coupled-cluster methods are calculated with respect to CCSD(T) CBS reference.
[c] Mean and max absolute errors of CCSD(T) reference are with respect to the experimental value.

TABLE III. Mean absolute errors (MAEs) and max absolute errors (MaxAEs) in eV for OAM24 dataset with respect to the NR2 CBS. CBS values are calculated by extrapolating aTZ and aQZ bases.

	MAE		MaxAE	
Basis set	NR2	NR2-F12	NR2	NR2-F12
aDZ	0.391	0.033	0.494[a]	0.056[a]
aTZ	0.159	0.015	0.204[a]	0.022[b]
aQZ	0.067		0.086[a]	

[a]Maleic anhydride.
[b]F_4-pDCNB.

most 0.002 eV and 0.001 eV on average, i.e., completely negligible. The GF2 and NR2 CBS IPs for the O21 and OAM24 sets were calculated by two-point X^{-3} extrapolation[66] using the {aQZ,a5Z} and {aTZ,aQZ} basis set pairs,respectively.

The reference IPs were computed as the differences between the CCSD(T) energies of the cation and neutral species. For the O21 set, the CCSD(T) and RI-CCSD(T)$_{\overline{\text{F12}}}$ [for simplicity denoted CCSD(T)-F12][67–69] reference total energies were calculated using Orca electronic structure program package.[70] The geminal correlation exponents in CCSD(T)-F12 computations were set to 1.1 and 1.2 for the aDZ and aTZ bases, respectively.[71] The Hartree-Fock and correlation energies were extrapolated separately using the {aTZ,aQZ} bases via the $e^{-X\alpha}$ and $X^{-\beta}$ schemes, respectively.[66,72] CCSD(T) CBS IPs for the OAM24 dataset were taken from Ref. 51.

The EOM-IP-CCSD calculations are performed using the parallel implementation in MPQC version 4. The aug-cc-pVXZ family of basis set were used and extrapolated using the standard two-point X^{-3} formula. CBS IP of the O21 set were calculated from aTZ and aQZ basis, while for OAM24, aDZ and aTZ bases were used. All IPs (in eV) calculated using GF and coupled cluster methods for O21 and OAM24 can be found in the supplementary material.

TABLE IV. Differences of IP in eV of OAM24 dataset calculated with GF and coupled-cluster methods and aXZ (X = D,T) basis relative to CCSD(T) CBS values from Ref. 51.

		GF2-F12		NR2-F12		EOM-IP-CCSD			CCSD(T)	
	Molecule	aDZ	aTZ	aDZ	aTZ	aDZ	aTZ	CBS[a]	CBS	Expt.
Acenes	Anthracene	−0.313	−0.309	0.009	0.024	−0.235	−0.101	−0.045	7.52	7.44
	Acridine	−0.347	−0.341	−0.025	−0.006	−0.247	−0.105	−0.045	8.04	7.8
	Phenazine	−0.339	−0.344	−0.028	−0.010	−0.228	−0.082	−0.021	8.47	8.44
	Azulene	−0.371	−0.364	−0.043	−0.023	−0.300	−0.161	−0.102	7.55	7.42
Quinones	Benzoquinone	−0.831	−0.807	−0.102	−0.077	−0.227	−0.001	0.094	10.27	10.0
	Naphthalenedione	−0.192	−0.189	−0.039	−0.021	−0.158	−0.018	0.041	9.88	9.5
	Dichlone	−0.273	−0.285	0.116	0.103	−0.020	0.112	0.167	9.99	9.5
	F_4-benzoquinone	−0.150	−0.158	0.305	0.308	−0.094	0.096	0.177	11.14	10.7[b]
	Cl_4-benzoquinone	−0.157	−0.184	0.244	0.207	−0.148	0.010	0.076	10.25	9.74[b]
Nitro/nitriles	Nitrobenzene	−0.129	−0.127	0.124	0.138	−0.138	0.002	0.061	10.19	9.94
	F_4-pDCNB	−0.228	−0.231	0.239	0.249	−0.161	0.025	0.104	10.76	10.65
	Dinitrobenzonitrile	0.032	0.032	0.322	0.335	−0.058	0.103	0.170	11.15	N/A
	Nitrobenzonitrile	−0.091	−0.090	0.232	0.248	−0.128	0.030	0.097	10.62	10.59
	Benzonitrile	−0.212	−0.208	0.076	0.092	−0.201	−0.054	0.008	9.93	9.73
	Fumaronitrile	−0.104	−0.100	0.114	0.127	−0.137	0.028	0.098	11.48	11.3[c]
	mDCNB	−0.173	−0.169	0.127	0.143	−0.186	−0.031	0.034	10.45	10.2
	TCNE	−0.037	−0.035	0.306	0.317	−0.076	0.099	0.172	11.99	11.79[b]
	TCNQ	−0.096	−0.092	0.194	0.213	−0.133	0.036	0.107	9.57	N/A
Anhydrides	Maleic anhydride	−0.113	−0.101	−0.090	−0.051	−0.306	−0.059	0.044	11.33	11.07[c]
	Phthalimide	−0.065	−0.058	0.110	0.140	−0.057	−0.017	0.000	10.08	9.90[c]
	Phthalic anhydride	−0.131	−0.126	0.147	0.162	−0.149	−0.004	0.056	10.55	10.1[b]
	Cl_4-isobenzofuranedione	−0.139	−0.170	0.296	0.265	−0.150	0.000	0.064	10.05	10.8
	NDCA	−0.229	−0.225	0.122	0.138	−0.210	−0.061	0.002	9.14	8.92
Other	Bodipy	−0.163	−0.156	0.072	0.097	−0.230	−0.076	−0.011	8.07	N/A
	MAE[d]	0.205	0.204	0.145	0.146	0.166	0.055	0.075	0.27[e]	
	MaxAE[d]	0.831	0.807	0.322	0.335	0.306	0.161	0.177	0.75[e]	

[a]CBS value calculated by the X^{-3} extrapolation of aDZ and aTZ IPs.
[b]Adiabatic IP.
[c]Vertical IP.
[d]Mean and max errors relative to the CCSD(T) CBS values.
[e]Errors relative to the experimental values.

IV. RESULTS AND DISCUSSION

The mean and maximum absolute basis set errors of NR2 and NR2-F12 IPs for the O21 set are listed in Table I. Already with a double-zeta basis the basis set error of the explicitly correlated NR2-F12 method is almost as good as the conventional quintuple-zeta NR2 counterpart. A triple-zeta basis is sufficient to converge the IPs to better than 0.05 eV.

Errors in GF2-F12, NR2-F12, CCSD(T)-F12, and EOM-IP-CCSD IPs with respect to the CBS CCSD(T) reference, along with the experimental values, for the O21 set are reported in Table II. As expected, NR2-F12 IPs are dramatically more accurate than the GF2-F12 IPs, with mean/max errors of only 0.14/0.26 eV vs 0.49/1.35 eV. However, NR2-F12 is less accurate than the more expensive CCSD(T)-F12 method. The closest counterpart to the NR2 approach is the EOM-IP-CCSD, whose cost is iterative $\mathcal{O}(N^6)$. The EOM-IP-CCSD CBS IPs are significantly more accurate than NR2-F12, with the former's mean absolute error (MAE) lower by more than a factor of 2. The maximum errors of these two methods are however comparable. It is notable that the largest deviations of EOM-IP-CCSD CBS IPs from the reference CCSD(T) CBS IPs are observed for *linear* molecules; this suggests that the unphysical loss of axial symmetry in the CCSD(T) treatment of ionized states might be at fault here and it is desirable to recompute the reference IPs using EOM-IP-CC with inclusion of triples to resolve the significant discrepancies between CCSD(T) and EOM-IP-CCSD.

The mean absolute and maximum basis set errors of NR2 and NR2-F12 IPs for the OAM24 set are listed in Table III. The NR2-F12 IPs with only a double-zeta basis are closer to the NR2 numerical limit than the conventional quadruple-zeta NR2 IPs. The aDZ basis is already sufficient to converge the NR2-F12 IPs to better than 0.05 eV.

Errors in GF2-F12, NR2-F12, CCSD(T)-F12, and EOM-IP-CCSD IPs with respect to the CBS CCSD(T) reference, along with the experimental values (where available), for the OAM24 set are reported in Table IV. The reference CCSD(T) CBS and experimental values of IP for OAM24 dataset are used from Ref. 51. We are not aware of any EOM-IP-CCSD data for the OAM24 dataset. The molecules are categorized into four groups and Bodipy to gauge the performance of methods for each subgroup of this dataset. Compared to the O21 set, here, the mean accuracy of GF2-F12 IPs is already quite high (~0.2 eV); however, the errors are systematically larger for acenes and a particularly large error (~0.8 eV) is observed for benzoquinone. NR2-F12 IPs are somewhat more accurate on average (~0.15 eV) and have a drastically reduced maximum error. EOM-IP-CCSD IPs are again significantly more accurate on average (~0.08 eV) than NR2-F12, albeit at a higher cost. It is also notable that the largest errors of EOM-IP-CCSD and NR2-F12 IPs are correlated: errors greater than 0.17 eV for EOM-IP-CCSD occur for the same 3 molecules for which NR2-F12 errors exceed 0.3 eV, and the signs for the errors agree in all cases. This suggests that perhaps again unphysical polarization in the CCSD(T) treatment of cations might be at fault here and higher-order EOM-IP-CC values are highly desired.

V. CONCLUSIONS

We presented a simple explicitly correlated (F12) extension of the renormalized second-order propagator (NR2) method for computing electron detachment energies. The NR2-F12 is characterized by greatly reduced basis set errors compared to the conventional NR2 method: precision of double-zeta basis NR2-F12 IPs is better than that of quadruple- or even quintuple-zeta NR2 IPs. Accuracy of NR2-F12 IPs is significantly higher than the nonrenormalized (non-diagonal) GF2-F12 IPs but is still substantially lower than that of EOM-IP-CCSD when assessed for two reference IP datasets (O21[60] and OAM24[51]). Nevertheless, NR2-F12 is a good starting point for higher-order models of superoperator/self-energy and can be an attractive alternative to EOM-IP-CCSD for well-behaved systems due to its noniterative (rather than iterative) $\mathcal{O}(N^6)$ cost. The EOM-IP-CCSD CBS IP estimates for the O21 and OAM24 datasets point out potential inaccuracies in the reference CCSD(T) CBS IP values and call for validation against higher-order EOM-IP-CC methods. Work along these lines is in progress.

SUPPLEMENTARY MATERIAL

See supplementary material for the numerical data used to produce Tables I–IV.

ACKNOWLEDGMENTS

N.K.T. and E.F.V acknowledge the support by the U.S. National Science Foundation (Grant Nos. 1550456 and 1800348). We thank the Advanced Research Computing (ARC) at Virginia Tech for providing the computing resources and support that contributed to this work.

REFERENCES

[1] D. J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic Press, New York, 1961).
[2] E. N. Economou, *Green's Functions in Quantum Physics* (Springer, 1983), Vol. 3.
[3] R. D. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem* (McGraw-Hill, 1967).
[4] J. Linderberg, Y. Öhrn, and A. C. Coulson, Proc. R. Soc. London, Ser. A **285**, 445 (1965).
[5] Y. Öhrn and J. Linderberg, Phys. Rev. **139**, A1063 (1965).
[6] J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry, Theoretical Chemistry* (Wiley, 2004).
[7] J. J. Phillips and D. Zgid, J. Chem. Phys. **140**, 241101 (2014).
[8] S. Hirata, M. R. Hermes, J. Simons, and J. V. Ortiz, J. Chem. Theory Comput. **11**, 1595 (2015).
[9] K. Bhaskaran-Nair, K. Kowalski, and W. A. Shelton, J. Chem. Phys. **144**, 144101 (2016).
[10] A. A. Rusakov and D. Zgid, J. Chem. Phys. **144**, 054106 (2016).
[11] S. Hirata, A. E. Doran, P. J. Knowles, and J. V. Ortiz, J. Chem. Phys. **147**, 044108 (2017).
[12] R. Movassagh, G. Strang, Y. Tsuji, and R. Hoffmann, J. Math. Phys. **58**, 033505 (2017).
[13] B. Peng and K. Kowalski, J. Chem. Theory Comput. **14**, 4335 (2018).
[14] B. G. Janesko, T. M. Henderson, and G. E. Scuseria, J. Chem. Phys. **130**, 081105 (2009).
[15] Y. Ma, M. Rohlfing, and C. Molteni, J. Chem. Theory Comput. **6**, 257 (2010).
[16] A. A. Kananenka and D. Zgid, J. Chem. Theory Comput. **13**, 5317 (2017).
[17] J. W. Knight, X. Wang, L. Gallandi, O. Dolgounitcheva, X. Ren, J. V. Ortiz, P. Rinke, T. Körzdörfer, and N. Marom, J. Chem. Theory Comput. **12**, 615 (2016).
[18] A. Heßelmann, Phys. Rev. A **95**, 062513 (2017).
[19] J. V. Ortiz, Int. J. Quantum Chem. **44**, 1 (1992).
[20] J. V. Ortiz, J. Chem. Phys. **103**, 5630 (1995).

[21] T. Maier, M. Jarrell, T. Pruschke, and M. H. Hettler, Rev. Mod. Phys. **77**, 1027 (2005).
[22] G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet, and C. A. Marianetti, Rev. Mod. Phys. **78**, 865 (2006).
[23] T. N. Lan, A. A. Kananenka, and D. Zgid, J. Chem. Phys. **143**, 241102 (2015).
[24] T. N. Lan and D. Zgid, J. Phys. Chem. Lett. **8**, 2200 (2017).
[25] B. Pickup and O. Goscinski, Mol. Phys. **26**, 1013 (1973).
[26] L. S. Cederbaum, Theor. Chim. Acta **31**, 239 (1973).
[27] M. J. Haugh and J. H. Birely, J. Chem. Phys. **60**, 264 (1974).
[28] L. S. Cederbaum, J. Phys. B: At. Mol. Phys. **8**, 290 (1975).
[29] L. S. Cederbaum and W. Domcke, Adv. Chem. Phys. **36**, 205 (1977).
[30] L. S. Cederbaum, W. Domcke, J. Schirmer, and W. von Niessen, Phys. Scr. **21**, 481 (1980).
[31] W. von Niessen, J. Schirmer, and L. Cederbaum, Comput. Phys. Rep. **1**, 57 (1984).
[32] J. Ortiz, Chem. Phys. Lett. **134**, 366 (1987).
[33] W. von Niessen, J. Chem. Phys. **67**, 4124 (1999).
[34] J. V. Ortiz, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **3**, 123 (2013).
[35] W. Kutzelnigg, Theor. Chim. Acta **68**, 445 (1985).
[36] W. Klopper, F. R. Manby, S. Ten-No, and E. F. Valeev, Int. Rev. Phys. Chem. **25**, 427 (2006).
[37] P. M. Gill and H. J. Werner, Phys. Chem. Chem. Phys. **10**, 3318 (2008).
[38] T. Shiozaki, E. F. Valeev, and S. Hirata, *Annual Reports in Computational Chemistry* (Elsevier, 2009), pp. 131–148.
[39] D. P. Tew and W. Klopper, Mol. Phys. **108**, 315 (2010).
[40] C. Hättig, D. P. Tew, and A. Köhn, J. Chem. Phys. **132**, 231102 (2010).
[41] L. Kong, F. A. Bischoff, and E. F. Valeev, Chem. Rev. **112**, 75 (2012).
[42] C. Hättig, W. Klopper, A. Köhn, and D. P. Tew, Chem. Rev. **112**, 4 (2012).
[43] S. Ten-no and J. Noga, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **2**, 114 (2012).
[44] S. Ten-no, Theor. Chem. Acc. **131**, 1070 (2012).
[45] Y.-y. Ohnishi and S. Ten-no, J. Comput. Chem. **37**, 2447 (2016).
[46] C. M. Johnson, A. E. Doran, S. L. Ten-no, and S. Hirata, J. Chem. Phys. **149**, 174112 (2018).
[47] F. Pavošević, C. Peng, J. V. Ortiz, and E. F. Valeev, J. Chem. Phys. **147**, 121101 (2017); e-print arXiv:1708.06474.
[48] H. H. Corzo and J. V. Ortiz, *Advances in Quantum Chemistry* (Elsevier, 2017), Vol. 74, pp. 267–298.
[49] J. V. Ortiz, J. Chem. Phys. **108**, 1008 (1998).
[50] O. Dolgounitcheva, M. Díaz-Tinoco, V. G. Zakrzewski, R. M. Richard, N. Marom, C. D. Sherrill, and J. V. Ortiz, J. Chem. Theory Comput. **12**, 627 (2016).
[51] R. M. Richard, M. S. Marshall, O. Dolgounitcheva, J. V. Ortiz, J.-L. Brédas, N. Marom, and C. D. Sherrill, J. Chem. Theory Comput. **12**, 595 (2016).
[52] O. Goscinski and B. Lukman, Chem. Phys. Lett. **7**, 573 (1970).
[53] W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **107**, 432 (1997).
[54] W. Kutzelnigg and J. D. Morgan, J. Chem. Phys. **96**, 4484 (1992).
[55] A. J. May, E. Valeev, R. Polly, and F. R. Manby, Phys. Chem. Chem. Phys. **7**, 2710 (2005).
[56] E. F. Valeev, Chem. Phys. Lett. **395**, 190 (2004).
[57] F. Pavošević, P. Pinski, C. Riplinger, F. Neese, and E. F. Valeev, J. Chem. Phys. **144**, 144109 (2016).
[58] S. Kedžuch, M. Milko, and J. Noga, Int. J. Quantum Chem. **105**, 929 (2005).
[59] C. Peng, J. A. Calvin, F. Pavošević, J. Zhang, and E. F. Valeev, J. Phys. Chem. A **120**, 10231 (2016).
[60] H. H. Corzo, A. Galano, O. Dolgounitcheva, V. G. Zakrzewski, and J. V. Ortiz, J. Phys. Chem. A **119**, 8813 (2015).
[61] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).
[62] R. A. Kendall, T. H. Dunning, and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
[63] D. E. Woon and T. H. Dunning, J. Chem. Phys. **98**, 1358 (1993).
[64] F. Weigend, A. Köhn, and C. Hättig, J. Chem. Phys. **116**, 3175 (2002).
[65] K. E. Yousaf and K. A. Peterson, Chem. Phys. Lett. **476**, 303 (2009).
[66] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, Chem. Phys. Lett. **286**, 243 (1998).
[67] E. F. Valeev, Phys. Chem. Chem. Phys. **10**, 106 (2008).
[68] E. F. Valeev and T. Daniel Crawford, J. Chem. Phys. **128**, 244113 (2008).
[69] J. Zhang and E. F. Valeev, J. Chem. Theory Comput. **8**, 3175 (2012).
[70] F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **8**, e1327 (2018).
[71] K. A. Peterson, T. B. Adler, and H.-J. Werner, J. Chem. Phys. **128**, 084102 (2008).
[72] F. Neese and E. F. Valeev, J. Chem. Theory Comput. **7**, 33 (2011).