Consistent ground states and renormalizations in *ab initio* propagator theory of molecules

J. V. Ortiz
Department of Chemistry and Biochemistry
Auburn University
www.auburn.edu/cosam/JVOrtiz

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Two RPA Themes in Quantum Chemisty

Antisymmetrized geminal power: consistent state function for RPA

$$|AGP\rangle = (G\dagger)^N |vac\rangle$$

$$G\dagger = \tfrac{1}{2} \sum_{j,k} c_{jk}\, b_j\dagger\, b_k\dagger$$

$$EAGP = \langle AGP|H|AGP\rangle / \langle AGP|AGP\rangle$$

Effects of RPA renormalizations in propagator calculations of molecular electron binding energies

AGP Wavefunctions

- Introduced to quantum chemistry by Coleman, Kutzelnigg, Silver, Bratoz, Durand, Bessis and Espaquet
- Antisymmetrized geminal power wavefunctions: state function for RPA with exchange that satisfies killer condition (Linderberg and Öhrn)
- Diatomic potential energy curves (Weiner, Jensen, Ortiz, Kurtz, Sangfelt, Chowdhury, Edwards, Zerner and Öhrn)
- Numerical problems in variational optimizations of larger molecules
- Restricted, singlet geminals used

Geminal Parametrization

Antisymmetrized geminal power: consistent state function for RPA

$$|AGP\rangle = (G^\dagger)^N |vac\rangle$$

Noncanonical form in orthonormal, generalized spin-orbital (GSO) basis of rank r:

$$G^\dagger = \tfrac{1}{2} \sum_{j,k}^{r} c_{jk} \, b_j^\dagger \, b_k^\dagger$$

$$c_{jk} = -c_{kj}$$

$$[b_j , b_k^\dagger] = 0$$

$$r = 2s$$

GSOs may be complex and have α and β spin components

Natural Form of Geminal

Geminal:

$$g(1,2) = \tfrac{1}{2} \sum_{j,k} r_{jk} \left[\tfrac{1}{2}\det\{\varphi_j(1)\varphi_k(2)\}\right]$$

Form natural GSOs with

$$\mathbf{U}^\dagger \mathbf{c}\mathbf{c}^\dagger \mathbf{U} = \mathbf{n}$$

n is diagonal and the eigenvalues are at least doubly-degenerate

Resulting natural expansion ($\boldsymbol{\varphi}\mathbf{U}=\boldsymbol{\chi}$) merely has the same first-order reduced density matrix for geminal – ***insufficient to recover any g***

Canonical, Natural Form of Geminal

Instead, using Zumino's theorem, one may construct a unitary matrix **W** such that

$$\mathbf{W}c\mathbf{W}t = \begin{pmatrix} \mathbf{0} & \mathbf{n}^{1/2} \\ \mathbf{n}^{1/2} & \mathbf{0} \end{pmatrix}$$

Canonical natural GSOs: $\boldsymbol{\varphi W = \psi}$

Standard AGP Parametrization

Standard form of geminal in terms of complex, canonical coefficients (ζ_k) and 2X2 determinants ($|\chi_k\ \chi_{k+s}\rangle$) built from natural GSOs

$$|g\rangle = \Sigma_{k=1s}\ \zeta_k\ |\chi_k\ \chi_{k+s}\rangle$$

Canonical coefficients defined only up to a phase factor, for

$$|g\rangle = \Sigma_{k=1s}\ \zeta_k\ e^{-i\nu}\ |\chi_k\ e^{i\nu/2}\ \chi_{k+s}e^{i\nu/2}\rangle$$

Improved AGP Parametrization

Without loss of generality, one may write

$$|g\rangle = \Sigma_{k=1s}\ n_{k1/2}\ |\psi_k\ \psi_{k+s}\rangle$$

Canonical coefficients ($n_{k1/2}$) are positive square roots of eigenvalues of first-order reduced density operator of $|g\rangle$

Canonical, natural GSOs (ψ_k) are unique up to 2X2 unitary transformations

Symmetric Functions

Given that $|g\rangle = \Sigma_{k=1s}\ n_k^{1/2}\ |\psi_k\ \psi_{k+s}\rangle$

Construct normalization integral with symmetric functions of order N: $S_N(\{n_k\})$

$$\langle AGP|AGP\rangle = (N!)^2\ S_N$$

Example: N=2, s=4

$$S_2 =$$

$$n_1 n_2 + n_1 n_3 + n_1 n_4 + n_2 n_3 + n_2 n_4 + n_3 n_4$$

Form density matrices with $S_{N-1}(i)$, $S_{N-2}(ij)$

Example: for s=4

$$S_2(3) = n_1 n_2 + n_1 n_4 + n_2 n_4$$

$$S_2(13) = n_2 n_4$$

AGP Total Energy

Construct total energy with lower-order symmetric functions

$$\langle AGP|H|AGP\rangle = (N!)^2$$

$$\{\Sigma_j n_j S_{N-1}(j)[h_{jj} + h_{j+s\,j+s} + \langle j\, j+s||j\, j+s\rangle] +$$

$$\Sigma_{jk} n_{j1/2} n_{k1/2} S_{N-1}(jk)\langle j\, j+s||k\, k+s\rangle +$$

$$\Sigma_{jk} n_j n_k S_{N-2}(jk)\langle j\, k|||j\, k\rangle\}$$

where

$$\langle j\, k\, ||| j\, k\rangle = \langle j\, k\, ||\, j\, k\rangle + \langle j\, k+s\, ||\, j\, k+s\rangle + \langle j + s\, k\, ||\, j+s\, k\rangle + \langle j+s\, k+s\, ||\, j+s\, k+s\rangle$$

Vary $\{n_k\}$ and $\{\psi_k\}$ to minimize total energy

An N-Representable DMFT

Occupation numbers of AGP:

$$\nu k = nkSN\text{-}1(k)$$

Natural GSOs of AGP = $\{\psi k\}$

Coleman showed there exists a 1-to-1 mapping from {vk} to {nk}

Variational AGP energy: a density-matrix functional with generalized spin-orbitals

C70 Photoelectron Spectrum – *Ab Initio* Electron Propagator Theory

Final State	Koopmans	EPT	Expt. (eV)
2A2”	7.54	7.45	7.47
2E1”	7.60	7.47	7.47
2 A2’	8.06	7.63	7.68
2 E2’	8.48	7.94	7.96
2 E2”	8.58	8.09	8.12
2 E1’	8.82	8.42	8.43

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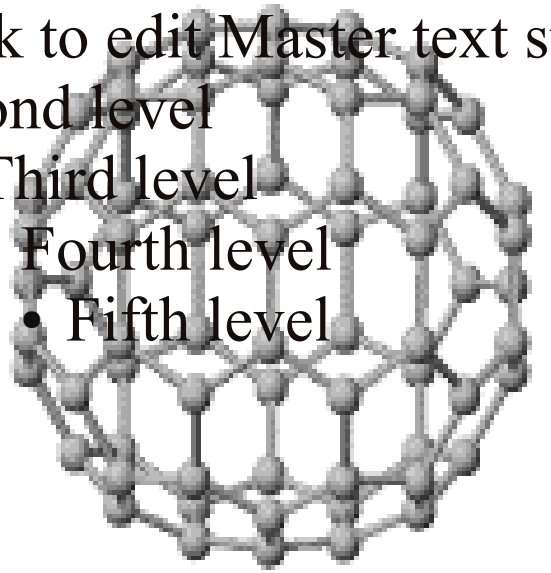
- Fifth level



One-electron Equations

Hartree Fock Theory

Hartree Fock Equations:

(Tkin + Unucl + JCoul - Kexch)φiHF ≡

F φiHF=εiHF φiHF

Same potential for all i:

core, valence, occupied, virtual.

εiHF includes Coulomb and exchange contributions to IEs and EAs

Electron Propagator Theory

Dyson Equation:

[F + ∑(εiDyson)]φiDyson = εiDyson φiDyson

Self energy, ∑(E): Energy dependent, nonlocal potential that varies for each electron binding energy

εiDyson includes Coulomb, exchange, relaxation and correlation contributions to IEs and EAs

φiDyson describes effect of electron detachment or attachment on electronic structure

Dyson Orbitals (Feynman-Dyson Amplitudes)

Electron Detachment (IEs)

$$\varphi i_{Dyson}(x1) =$$

$$N^{-1/2} \int \Psi N(x1,x2,x3,\ldots,xN) \Psi^{*}i,N-1(x2,x3,x4,\ldots,xN)$$

$$dx2dx3dx4\ldots dxN$$

Electron Attachment (EAs)

$$\varphi i_{Dyson}(x1) =$$

$$(N+1)^{-1/2} \int \Psi i,N+1(x1,x2,x3,\ldots,xN+1) \Psi^{*}N(x2,x3,x4,\ldots,xN+1)$$
$$dx2dx3dx4\ldots dxN+1$$

Pole strength – criterion for quasiparticle picture

$$Pi = \int |\varphi i_{Dyson}(x)|^2 dx$$

$$0 \leq Pi \leq 1$$

Dyson Orbitals and Photoionization Cross Sections

Differential Cross Sections:

$$d\sigma(\Theta)/d\Omega =$$

$$(me/\hbar 2)\,(L3kec/2\pi\omega A02)\,|\langle \varphi Dyson \mid Top\ \varphi cont \rangle|2$$

Continuum Orbital, φcont: Plane-wave or orthogonalized plane-wave

Transition Operator: Dipole or all-multipole expression,

$$Top = -(eA0n/me\ c)\Sigma j=1N\ eik(ph)*r(j)\ \ p(j)$$

Self-Energy Approximations and Solutions of Dyson Equation

I. Quasiparticle corrections to Koopmans results:

$$E = \varepsilon_i + \Sigma_{ii}(E)$$

II. Renormalized quasiparticle methods

$$E = \varepsilon_{iR} + \Sigma_{iiR}(E)$$

Quasiparticle picture is valid only when $P_i \approx 1$ and $\Sigma_{i \neq j}(E) \approx 0$

Approximate Dyson Equations

III. Renormalizations for strong relaxation & correlation effects: NR2, ADC(3), BD-T1

$$E\,\mathbf{C} = [\mathbf{F} + \mathbf{\Sigma}(E)]\mathbf{C}$$

$$\mathbf{\Psi}\text{Dyson} = \mathbf{\phi C}$$

$$P = [1 - \mathbf{C\dagger\Sigma'}(E)\mathbf{C}]\text{-}1$$

Renormalized Self-Energies

Solve: $E\,\mathbf{C} = [\mathbf{F} + \mathbf{\Sigma}(E)]\mathbf{C}$

Alternatively, solve $\hat{\mathbf{H}}\,\mathbf{X} = \mathbf{X}\,E$, where

$$\mathbf{F} = \hat{\mathbf{H}}aa$$

$$\mathbf{\Sigma}(E) = \hat{\mathbf{H}}af\,(E\mathbf{1} - \hat{\mathbf{H}}ff\,)\text{-}1\hat{\mathbf{H}}fa$$

$$\hat{H}xy = \langle 0|[x\dagger,[y,H]]+|0\rangle$$

x and y belong to set of ionization operators:

{a,f} = {a,f3 ,f5,f7,...} = {a,aaa†,aaaa†a†,...}

Matrix Elements of $\hat{\mathbf{H}}$

Primary-primary (aa) block: generalized Fock matrix

$$\mathbf{F} = \hat{\mathbf{H}}^{aa}$$

$$F_{rs} = h_{rs} + \Sigma_{tu} [\langle rt|st\rangle - \langle rt|ts\rangle] \rho_{tu}$$

r,s,t,u – occupied or virtual spin-orbitals

Matrix Elements of $\hat{H}$

Primary-primary (aa) block:

First-order approximation

$$\rho_{tu} = n_t \delta_{tu}$$

n_t = occupation numbers in reference determinant

HF-CMO basis: $F_{rs} = \varepsilon_r^{HF} \delta_{rs}$

KS-CMO basis: $F_{rs} = \varepsilon_r^{KS} \delta_{rs} - \Delta V_{rs}$

where $\Delta V_{rs} = v_{xc}^{rs} + \Sigma_t \langle rt|ts \rangle n_t$

Matrix Elements of $\hat{H}$

Primary-secondary (af and fa) blocks: $\hat{H}_{af}$

$f \approx f3 = aaa^\dagger$ operators

First-order expressions:

2hp: $a_i a_j a_b^\dagger$ where i,j occupied and b virtual

$\langle pb|ij\rangle - \langle pb|ji\rangle = \hat{H}_{p,ijb}$

2ph: $a_b a_c a_i^\dagger$ where i occupied and b,c virtual

$\langle pi|bc\rangle - \langle pi|cb\rangle = \hat{H}_{p,bci}$

Matrix Elements of $\hat{H}$

Secondary-secondary (ff) block, $\hat{H}$ff

f3 = aaa† operators

First-order approximations:

2hp couplings: where i,j,k,l occupied and b,c virtual i for aiajab† and akalac†

$\hat{H}ijb,klc = (\varepsilon i + \varepsilon j - \varepsilon b)\delta ik\delta jl\delta bc$

$- \Delta Vjk\delta jl\delta ab - \Delta Vjl\ \delta ik\delta ab + \Delta Vab\ \delta ik\delta jl$

$- \langle ij||kl\rangle\delta ab$

$+ (1-Pij)(1-Pkl)\ \delta ik\langle bj||al\rangle$

2ph couplings: $\hat{H}bci,dej$ (ijkl → bcde ; bc → ij)

Familiar Approximations

$\hat{H}_{ijb,klc} = (\varepsilon_i + \varepsilon_j - \varepsilon_b)\delta_{ik}\delta_{jl}\delta_{bc}$

$- \Delta V_{jk}\delta_{jl}\delta_{ab} - \Delta V_{jl}\delta_{ik}\delta_{ab} + \Delta V_{ab}\delta_{ik}\delta_{jl}$

$- \langle ij||kl\rangle\delta_{ab}$

$+ (1-P_{ij})(1-P_{kl})\,\delta_{ik}(\langle bj|al\rangle - \langle bj|la\rangle)$

Ladders

RPA

$\hat{H}_{p,ijb} = \langle pb|ij\rangle - \langle pb|ji\rangle$

HF-CMO basis, retain all terms: **2ph-TDA**

KS semicanonical basis ($F_{bc} = \varepsilon_b \delta_{bc}$; $F_{ij} = \varepsilon_i \delta_{ij}$; $F_{ia} \neq 0$; $F_{ai} \neq 0$), neglect red terms: **GW**

Additional Approximations

$\hat{H}_{ijb,klc} = (e_i + e_j - e_b)\delta_{ik}\delta_{jl}\delta_{bc}$

$- \langle ij||kl\rangle \delta_{ab}$

$+ (1-P_{ij})(1-P_{kl})\, \delta_{ik}(\mathbf{\langle bj|al\rangle} - \mathbf{\langle bj|la\rangle})$

$\hat{H}_{p,ijb} = \langle pb|ij\rangle - \mathbf{\langle pb|ji\rangle}$

KS semicanonical basis: **KS-f3**

Neglect red terms: **KS-f3-RPA**

Neglect also RPA terms in $\hat{H}_{ijb,klc}$: **KS-2X**

Neglect also $\langle pb|ji\rangle$ term in $\hat{H}_{p,ijb}$: **KS-2**

Test Calculations

Vertical Ionization Energies < 20 eV

Test molecules: CO, N2, HF, H2O, F2, C2H4

KS approximations: B3LYP, SVWN, LSDA

Basis set: cc-pVQZ

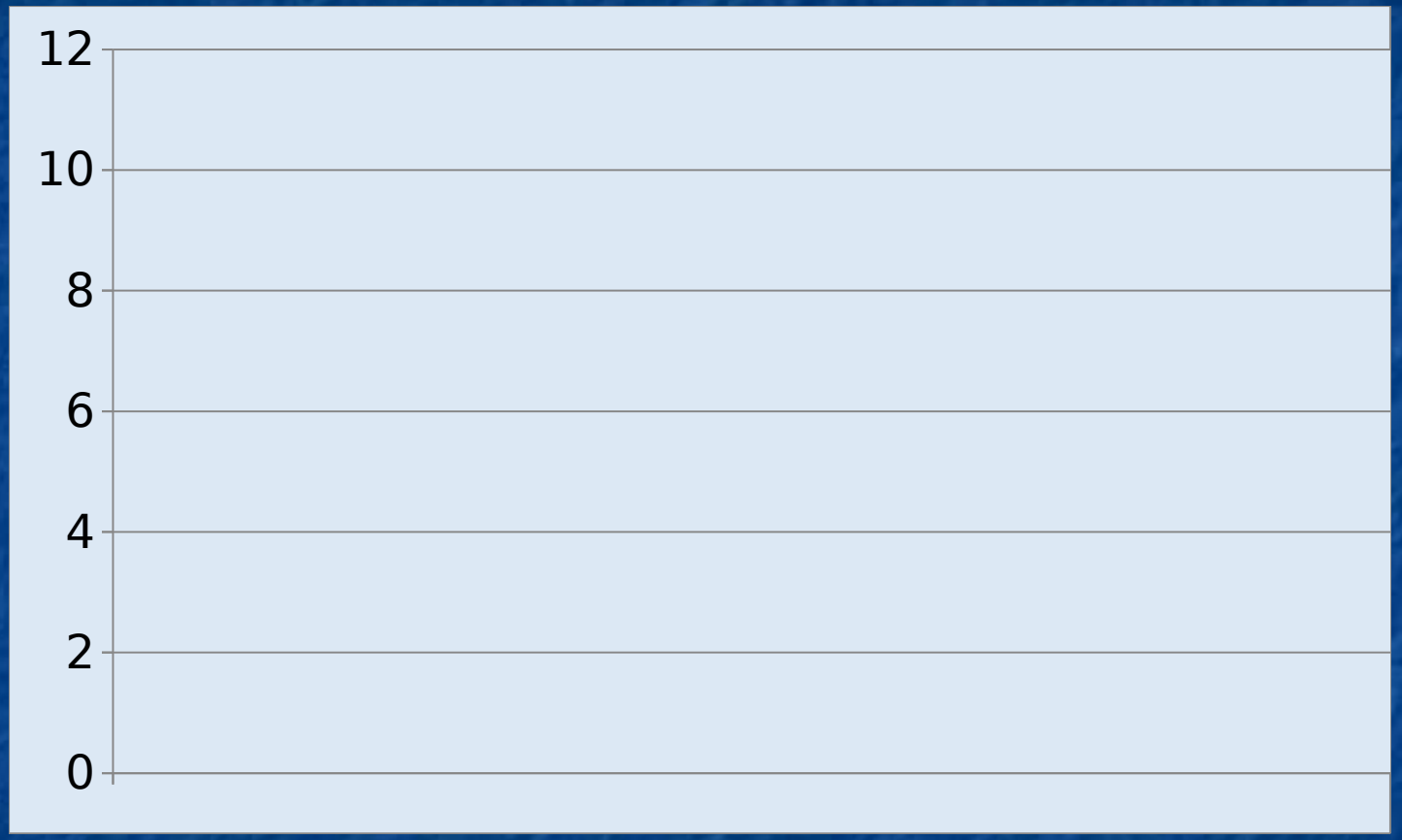
Comparison: KS orbital energy,

semicanonical KS orbital energy (ei),

KS-f3, KS-f3-RPA, KS-2X, KS-2

HF-based approximations: ADC(3), NR2

Mean Absolute Deviations (eV)



ADC(3): MAD = 0.26 eV

NR2: MAD = 0.18 eV

Test Calculations: Conclusions

Ladder terms are needed to balance RPA terms

Pole strengths decline markedly in KS-f3-RPA

Best cancellation of errors for KS-2:

semicanonical orbital energies

no exchange terms

(Mark Casida: MAD ~ 0.5 eV with HF orbitals)

Inclusion of exchange, ladders and RPA:

reasonable results for KS-2X, KS-f3

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