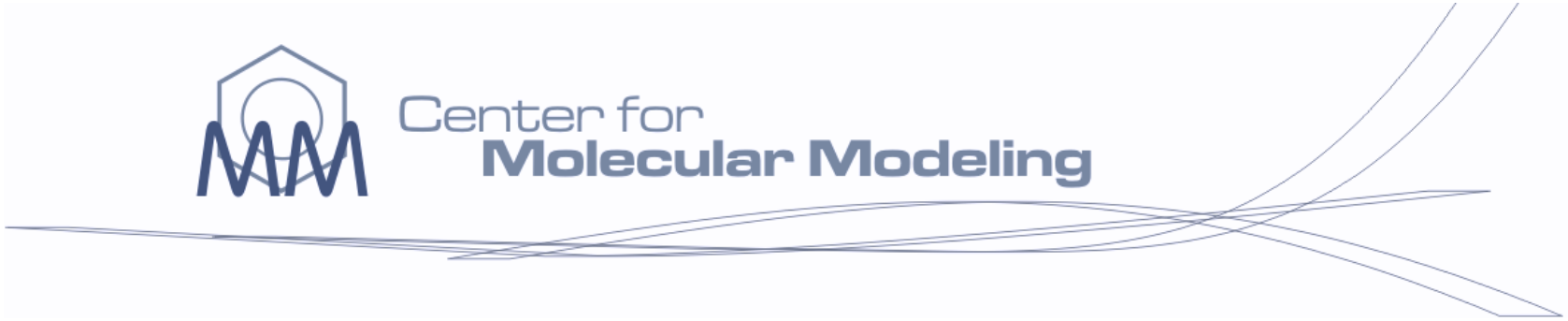

Faddeev Random Phase Approximation (FRPA) Application to Molecules

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INT 2011 Spring Program
Fermions from Cold Atoms to Neutron Stars:
Benchmarking the Many-Body Problem

Outline

What is FRPA?

It is a Green's function method that uses
Faddeev equations to couple
Random Phase Approximation (RPA) interactions
in a consistent way and to sum them to an infinite order

Situating the problem

Hamiltonian

Within the Born-Oppenheimer approximation

$$\hat{H} = \hat{T} + \hat{U}_{ext} + \hat{V}_{ee}$$

- only 2-body interactions
- interactions are known

$\hat{T}$ kinetic energy
$\hat{U}_{ext}$ central potential due to nuclei
$\hat{V}_{ee}$ Coulomb-repulsion between electrons

Situating the solution

Green's functions

In the time domain

$$G_{\alpha,\beta}(t-t') = \frac{-i}{\hbar}\left\langle \Psi_0^N \middle| \mathcal{T}\left(a_\alpha(t)a_\beta^\dagger(t')\right) \middle| \Psi_0^N \right\rangle$$

- propagation of single partice states from time t to t'

Lehmann-representation

$$G_{\alpha,\beta}(E) = \sum_n \frac{\left\langle \Psi_0^N | a_\alpha | \Psi_n^{N+1} \right\rangle \left\langle \Psi_n^{N+1} \middle| a_\beta^\dagger \middle| \Psi_0^N \right\rangle}{E-(E_n^{N+1}-E_0^N)+i\eta} + \sum_m \frac{\left\langle \Psi_0^N \middle| a_\beta^\dagger \middle| \Psi_m^{N-1} \right\rangle \left\langle \Psi_m^{N-1} | a_\alpha | \Psi_0^N \right\rangle}{E-(E_0^N-E_m^{N-1})-i\eta}$$

- transition amplitudes
- excitation energies

Perturbation expansion

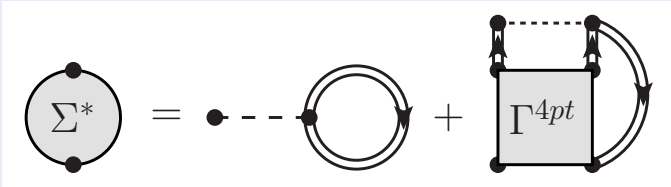
Dyson equation

$$G(E) = G_0(E) + G_0(E)\Sigma^*(E)G(E)$$

Irreducible Self-Energy and higher-order vertex functions

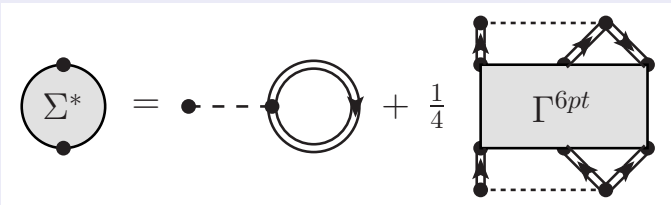
$$\Sigma^*(E) = \Sigma_{HF} + M(E)$$

- 4-point function



  Examples: GW, Bold Diagrammatical Monte Carlo, T-matrix

- 6-point function



  Examples: ADC(3), FRPA, all the previous examples

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Algebraic diagrammatic construction

Algebraic diagrammatic construction

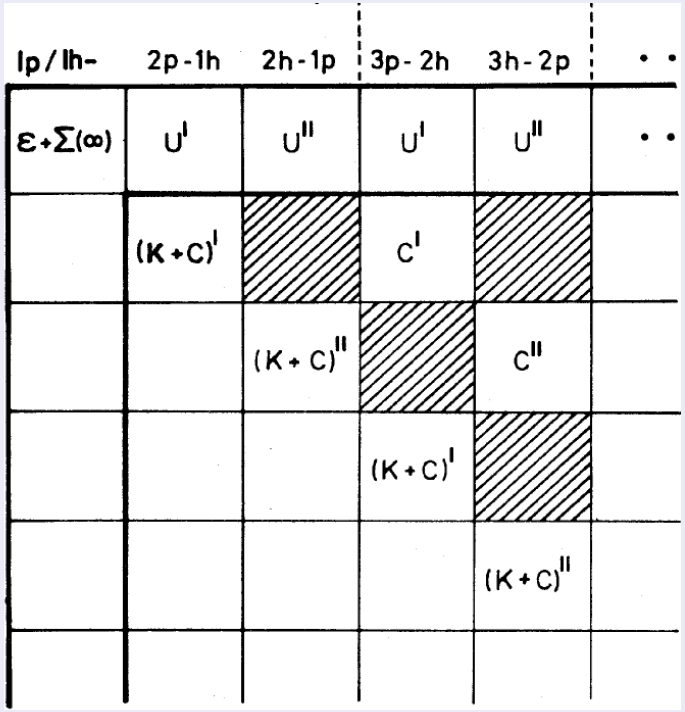
Schirmer et al. Phys. Rev. A 28 (1983)

$M(E) = U^\dagger \frac{1}{E-K-C+i\eta} U$

- only depends on 1 energy
- expand U and C in orders
  $U = U^{(1)} + U^{(2)} + \ldots$
  $C = C^{(1)} + C^{(2)} + \ldots$
- exact up to certain order
- formulated as an expansion in Coulomb matrix elements
- coupling to 1p2h, 2p3h, ...

Algebraic diagrammatic construction

Matrix structure



- Indirect coupling of 2p1h and 2h1p
- matrix size grows every 2 orders

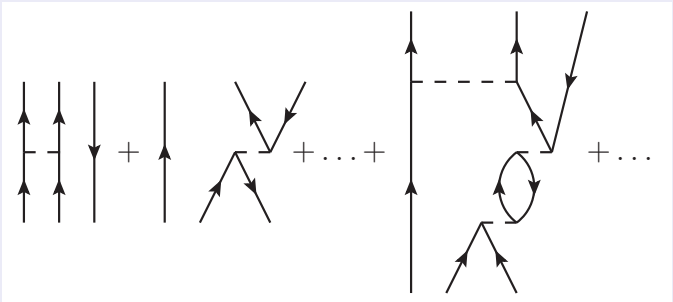
ADC(3)

Third order ADC

- coupling between single particle states and 2p1h/2h1p
- consisent up to third order
- compromise between speed and precision
- good ground state energies and ionization energies

Interpretation

- equation of motion (EOM)
  $Q^n_{p_1 p_2 h} = a^\dagger_{p_1} a^\dagger_{p_2} a_h$
- diagrammatic
  - infinite resummation
  - interactions between two of the three lines
  - only 3 states at any energy



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TDA and RPA

- ADC(3) is equivalent to exchange of Tamm Dancoff (TDA) phonons
- not clear how!

TDA

- approximation for ph and 2p propagator
- no mixture between forward and backward propagation

RPA

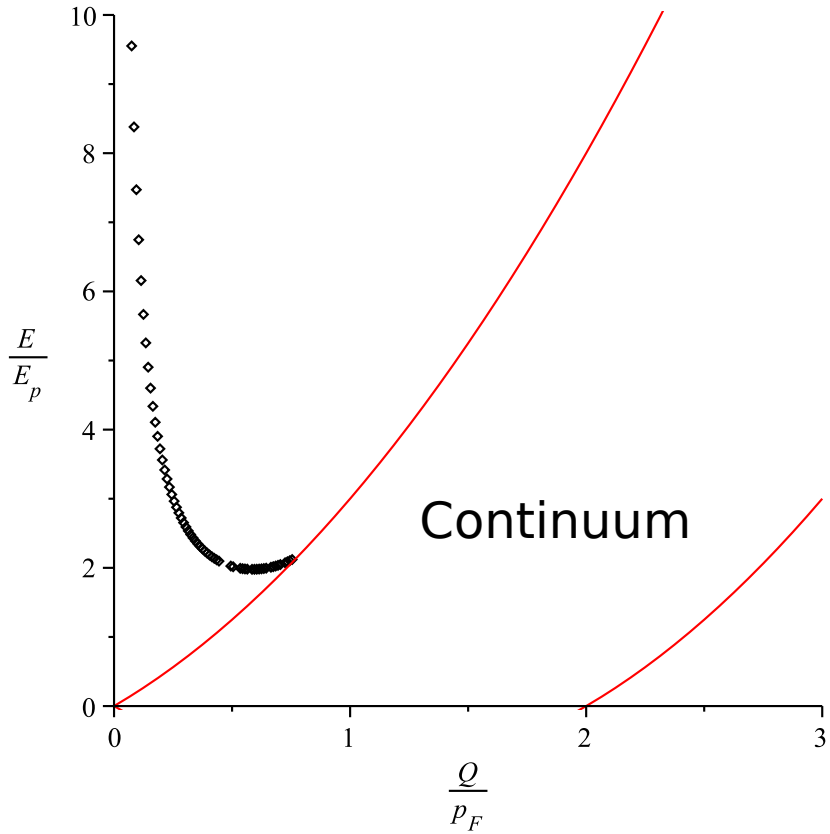
- dynamically screens interaction
- used in condensed matter physics
- links forward and backward propagating amplitudes

$$\begin{pmatrix} A & B \\ B^* & C \end{pmatrix} \begin{pmatrix} \mathcal{X} \\ \mathcal{Y} \end{pmatrix} = sgn(\epsilon)\,\epsilon \begin{pmatrix} \mathcal{X} \\ \mathcal{Y} \end{pmatrix}$$

Advantages of RPA over TDA

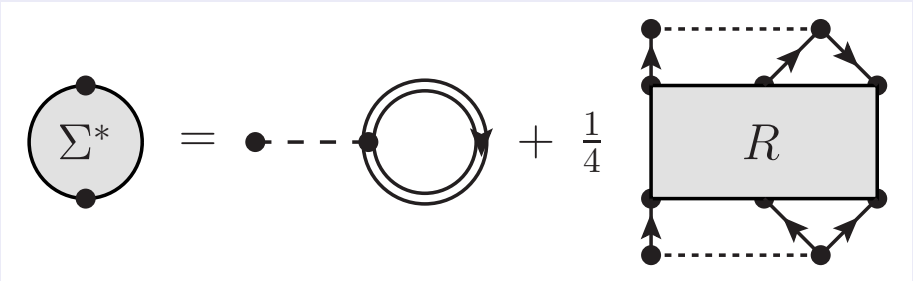
Random Phase Approximation

- improves over TDA by including mixture between positive and negative energy excitations
- example: plasmon pole in polarization propagator

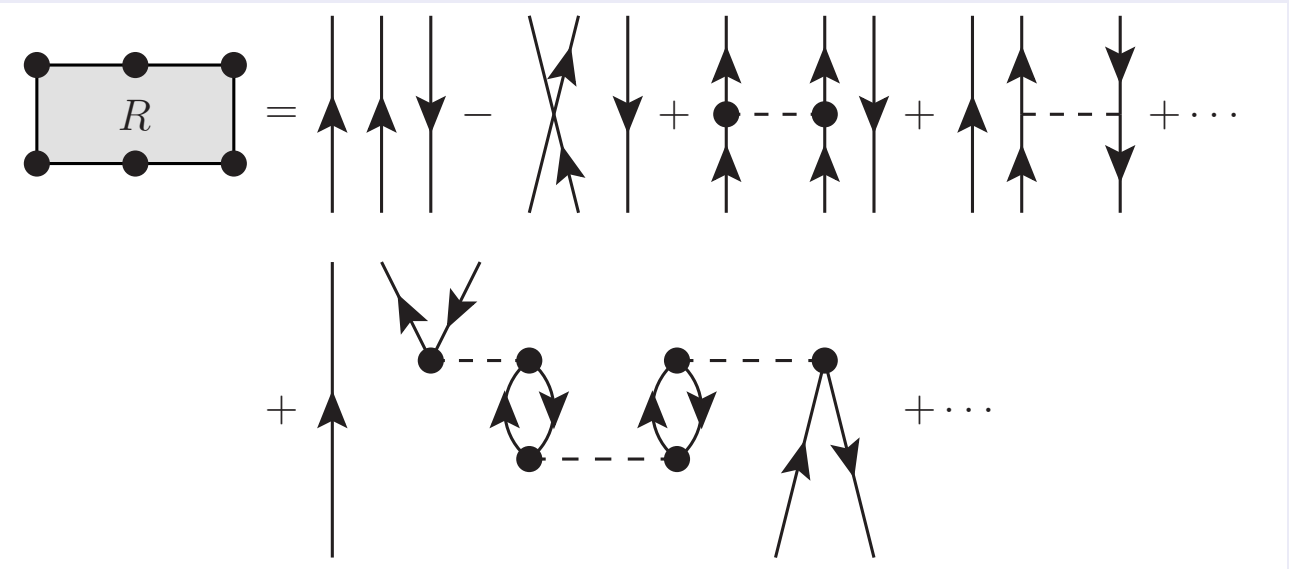


Diagrammatic content of FRPA

Dyson equation



FRPA 2p1h propagator



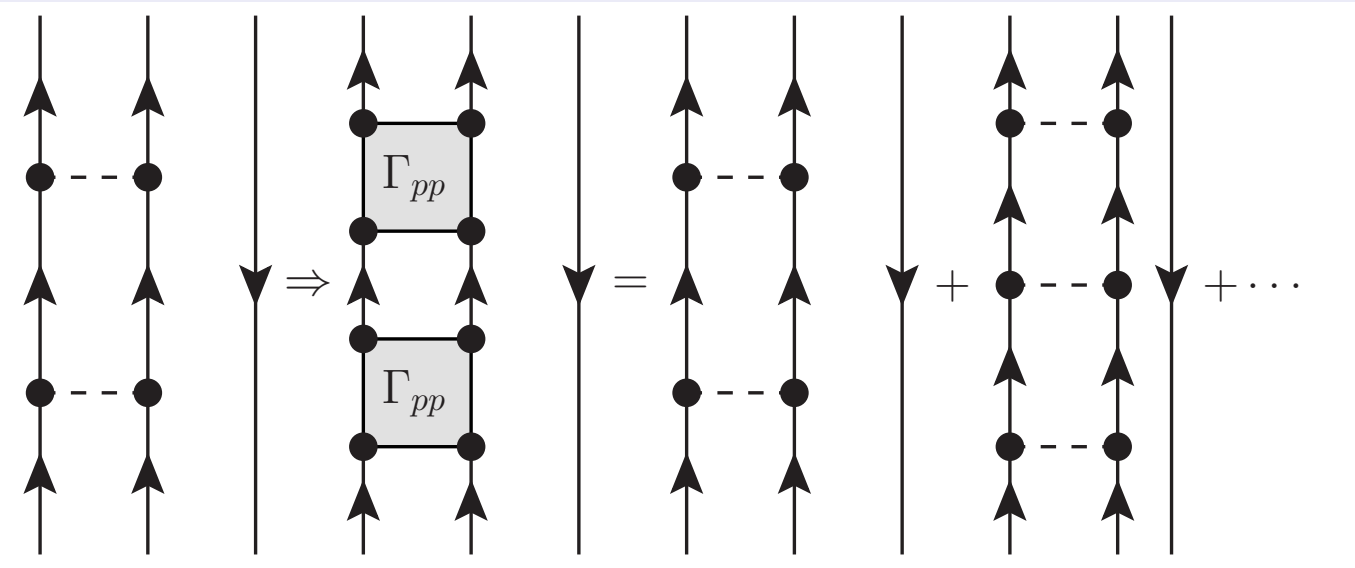
- no longer only 3 lines at every energy

Different approach

Difficulties

- no equivalent nth order expansion in Coulomb elements
- not just replacing interactions by screened RPA interactions

Double counting



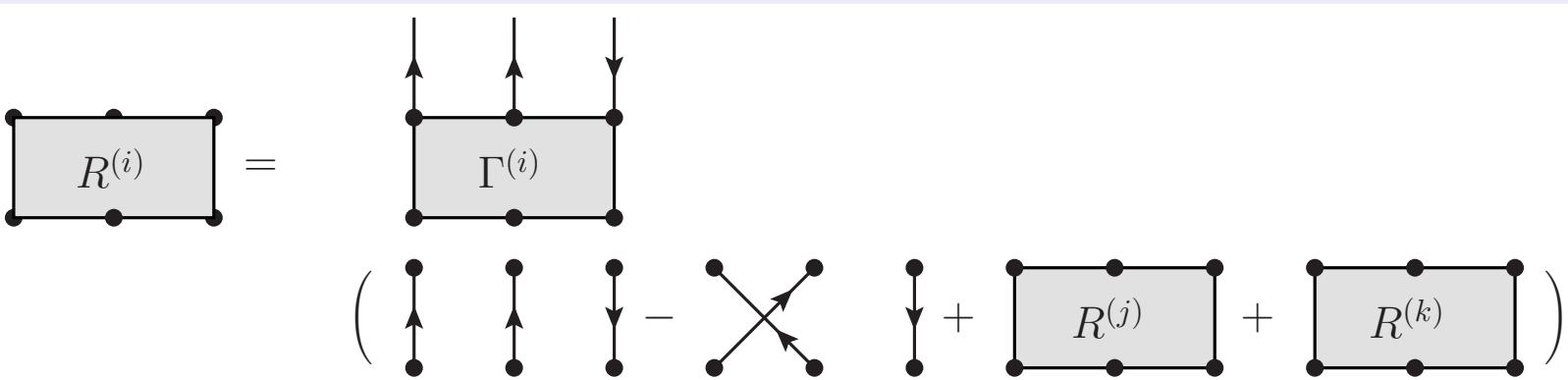
- no simple Bethe Salpeter equation possible

Introduction of Faddeev equations

Splitting up the propagator

- from 3-body problem
- but without three-body forces
- $R(E) = R_{free}(E) + \sum_{i=1..3} R^{(i)}(E)$

Interpretation of the parts



Line i propagates freely, $\Gamma^{(i)}$ is appropriate RPA interaction between line j and k

Faddeev equations

Matrix equations

- Lehmann-representation for $R^{(i)}$
- amplitudes and poles are found from eigenvalue-equation

$$\begin{pmatrix} 1 & -H^{(1)}H^{(1)\dagger} & -H^{(1)}H^{(1)\dagger} \\ -H^{(2)}H^{(2)\dagger} & 1 & -H^{(2)}H^{(2\dagger)} \\ -H^{(3)}H^{(3\dagger)} & -H^{(3)}H^{(3\dagger)} & 1 \end{pmatrix}^{-1} \begin{pmatrix} U^{(1)}D^{(1)}U^{(1)-1} & U^{(1)}T^{(1)\dagger} - U^{(1)}D^{(1)}U^{(1)-1}H^{(1)}H^{(1)\dagger} & U^{(1)}T^{(1)\dagger} - U^{(1)}D^{(1)}U^{(1)-1}H^{(1)}H^{(1)\dagger} \\ U^{(2)}T^{(2)\dagger} - U^{(2)}D^{(2)}U^{(2)-1}H^{(2)}H^{(2)\dagger} & U^{(2)}D^{(2)}U^{(2)-1} & U^{(2)}T^{(2)\dagger} - U^{(2)}D^{(2)}U^{(2)-1}H^{(2)}H^{(2)\dagger} \\ U^{(3)}T^{(3)\dagger} - U^{(3)}D^{(3)}U^{(3)-1}H^{(3)}H^{(3\dagger)} & U^{(3)}T^{(3)\dagger} - U^{(3)}D^{(3)}U^{(3)-1}H^{(3)}H^{(3\dagger)} & U^{(3)}D^{(3)}U^{(3)-1} \end{pmatrix} \begin{pmatrix} \mathcal{X}^{(1)} \\ \mathcal{X}^{(2)} \\ \mathcal{X}^{(3)} \end{pmatrix} = \epsilon \begin{pmatrix} \mathcal{X}^{(1)} \\ \mathcal{X}^{(2)} \\ \mathcal{X}^{(3)} \end{pmatrix}$$

- reduces to ADC(3) or FTDA when $H^{(i)} = 0$

Spurious solutions

- 3 times matrix dimension of 2p1h-space
  - $\Rightarrow$ 2/3 are spurious
    $\sum_{i=1..3} R^{(i)}(E) = 0$

FRPA recipe

FRPA properties

- infinite summation of diagrams through self-consistent equation
- conserving in Baym-Kadanoff manner
- ph- and pp-channels treated equivalently
- non-hermitian eigenvalue equation for 2p1h/2h1p amplitudes and energies
  - $\Rightarrow$ complex eigenvalues are possible
- iterative treatment of static self-energy

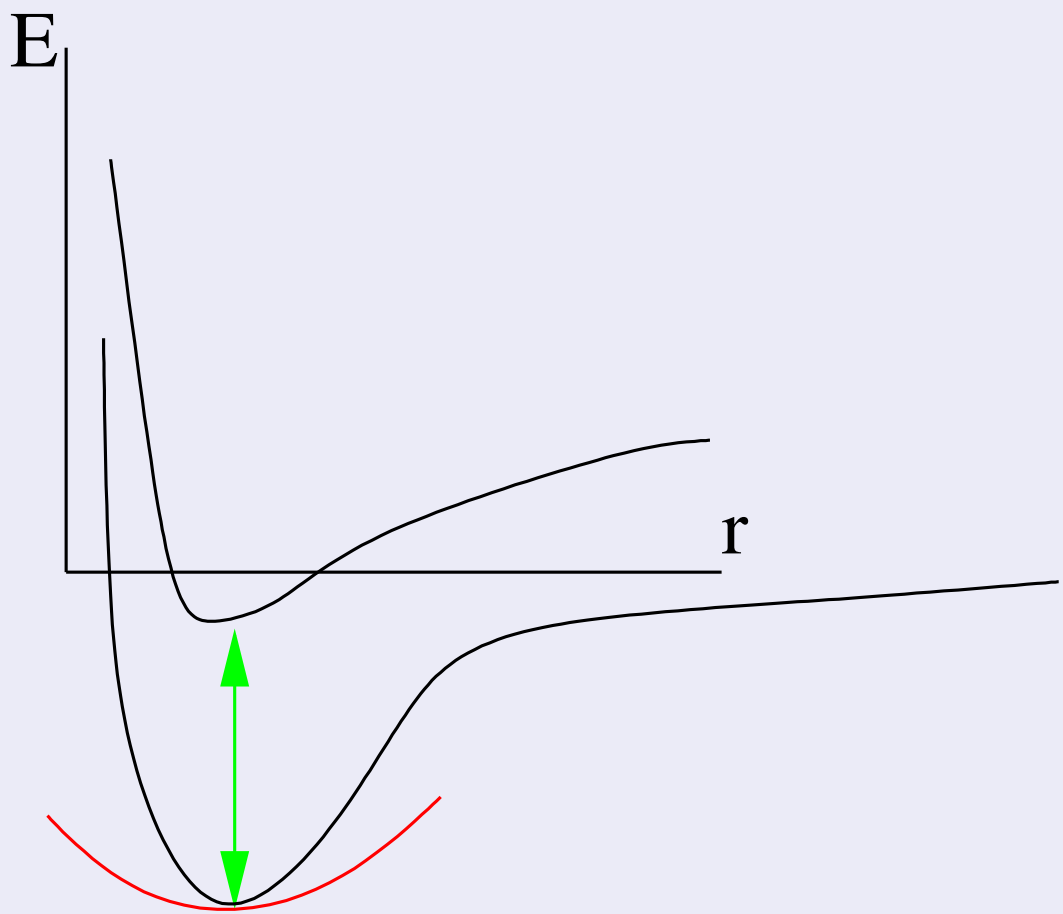
$$F = \begin{array}{c} \\ \text{p/h} \\ \text{2p1h} \\ \text{2h1p} \end{array} \begin{array}{c} \begin{array}{ccc} \text{p/h} & \text{2p1h} & \text{2h1p} \end{array} \\ \begin{pmatrix} \epsilon & \tilde{U} & \tilde{U} \\ \tilde{U}^\dagger & \epsilon^{Fd} & 0 \\ \tilde{U}^\dagger & 0 & \epsilon^{Fd} \end{pmatrix} \end{array}$$

- same U as in ADC(3)

Calculations

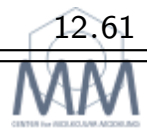
Calculated properties for linear molecules

- ground-state energies
- vertical ionization energies
- bond lengths



Ground state properties

Molecule		FTDA	FRPA	CCSD(T)	FCI	Expt.
H_2						
	E_0	−1.161	−1.161	−1.164	−1.164	−1.175
	r_{H-H}	0.757	0.757	0.761		0.741
	I	16.03	16.03	16.12		16.08
HF						
	E_0	−100.224	−100.228	−100.228	−100.231	-
	r_{H-F}	0.916	0.913	0.920		0.917
	I	15.70	15.54	15.42		16.12
HCl						
	E_0	−460.256	−460.255	−460.254		-
	r_{H-Cl}	1.297	1.293	1.290		1.275
	I	12.24	12.24	12.26		-
BF						
	E_0	−124.365	−124.368	−124.380		-
	r_{B-F}	1.284	1.285	1.295		1.267
	I	10.75	10.94	11.01		-
BeH_2						
	E_0	−15.831	−15.832	−15.835	−15.836	-
	r_{Be-H}	1.337	1.337	1.339		1.340
	I	11.78	11.76	11.89		-
H_2O						
	E_0	−76.240	−76.236	−76.241		-
	r_{H-O}	0.964	0.962	0.967		0.958
	Λ_{O-H-O}	102	102	102		104
	I	12.15	12.21	11.94		12.61



calculated in cc-pVDZ

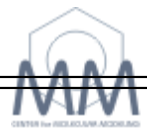
Ground state properties

Molecule		FTDA	FRPA	CCSD(T)	FCI	Expt.
N_2						
	E_0	−109.258	−109.272	−109.276		-
	r_{N-N}	1.104	1.106	1.119		1.098
	I	15.37	14.80	15.05		15.58
CO						
	E_0	−113.037	−113.048	−113.055		-
	r_{C-O}	1.130	1.123	1.145		1.128
	I	13.69	14.44	13.64		14.01
CO_2						
	E_0	−188.139	−188.134	−188.148		-
	r_{C-O}	1.162	1.162	1.175		1.162
	I	13.25	13.42	13.26		13.78
C_2H_2						
	E_0	−77.102	−77.093	−77.111		-
	r_{C-C}	1.298	1.298	1.232		1.203
	r_{C-H}	1.083	1.080	1.081		1.063
	I	11.26	11.14	11.08		11.49

calculated in cc-pVDZ

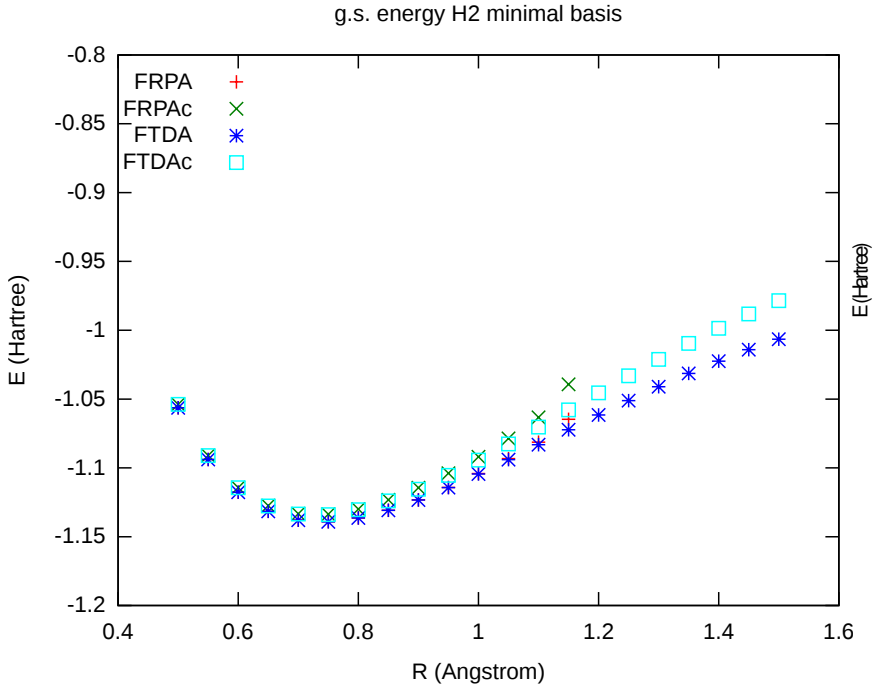
Vertical ionization energies

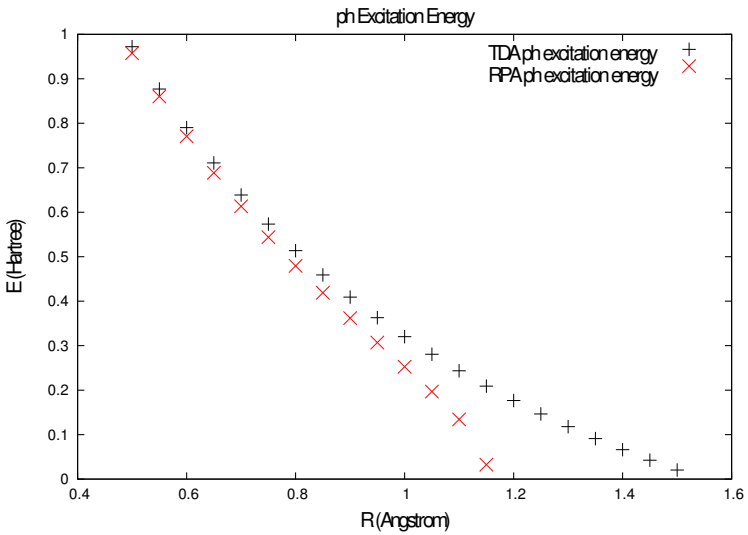
Molecule	Level	HF	FTDA	FRPA	Expt.
HF					
	1π	17.17	16.46	16.35	16.05
	3σ	20.98	20.33	20.24	20.0
CO					
	5σ	15.10	13.88	13.69	14.01
	1π	17.44	16.93	16.84	16.91
	4σ	21.99	20.11	19.59	19.72
N_2					
	$3\sigma_g$	17.25	15.65	15.18	15.60
	$1\pi_u$	16.73	16.82	17.14	16.98
	$2\sigma_u$	21.25	18.99	17.90	18.78
H_2O					
	$1b_1$	13.86	12.83	12.67	12.62
	$3a_1$	15.93	15.11	14.98	14.74
	$1b_2$	19.56	19.19	19.13	18.51
	$\bar{\Delta}$ (eV)	1.26 (1.14)	0.27 (0.28)	0.31 (0.26)	
	Δ_{max} (eV)	2.47 (2.27)	0.68 (0.68)	0.88 (0.62)	



calculated in aug-cc-pVDZ at experimental geometry

Problems in the dissociation limit





RPA instability H_2 in minimal basis set

essentially the same as 2-site Fermi-Hubbard at half-filling

- ground state is combination of Slater-determinants
- ph excitation lower in energy
- Fermi-Hubbard
  - TDA linear behavior $\Rightarrow$ becomes negative
  - RPA square root behavior $\Rightarrow$ becomes complex

Conclusion

Dissociation limit not feasible

- only good in situations where Hartree-Fock is reasonable
- may be solved by including fragmentation
  Dewulf et al. Phys. Rev. C 65 (2002)
- use of other phonons

In general

- no over-correlation
- works for nuclei, atoms, molecules
- should work for extended systems (electron gas, H-chains, schematic models,...)
- can be improved by better self-consistency
- speed can be improved by partial diagonalization with Lanczos-algorithm

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