



Resonating Valence Bond wave function with molecular orbitals: application to diatomic molecules

M. Marchi^{1,2}, S. Azadi², M. Casula³, S. Sorella^{1,2}

¹ DEMOCRITOS, National Simulation Center, 34014, Trieste, Italy.

² SISSA, International School for Advanced Studies, 34014, Trieste, Italy.

³ Centre de Physique Théorique, École Polytechnique, CNRS, 91128 Palaiseau, France.

Outline



- Brief introduction
- JAGP wave function
- Constrained optimization of molecular orbitals
- Test and applications:
 1. Be_2 : a challenging molecule!
 2. F_2
 3. Results for dimers composed of first-row atoms
 4. Determination of Fe_2 ground state
- Conclusions

Introduction



- **Goal:** Accurate description of chemical bond with minor computational effort.
- **Framework:** QMC simulations and correlated antisymmetrized geminal power wave function (JAGP) (based on Pauling's resonating valence bond idea)
- **Techniques:** optimization techniques (stochastic reconfiguration with Hessian acceleration), VMC, LRDMC (pseudopotentials to eliminate valence core electrons) and JAGP with molecular orbitals (constrained optimization).

Trial wave functions



N-electron system:

$$\Psi = \Phi_N J$$

- Φ_N accounts for statistical correlations and determines the nodes
- J accounts for so-called 'dynamical' correlations.

RVB wave functions



- **Pauling**: chemical valence bond described as **(singlet) pair** of electrons and the true quantum state of a compound is the superposition or **resonance** of many valence-bond states.
The superposition usually improves the variational energy of the state.
L. Pauling, Phys. Rev. 54, 899 (1938)
Example: Benzene
- **Anderson** further developed this idea to study high-temperature superconductors
- **Bouchaud and Lhuillier** applied it in a MC study of 3 He

AGP ansatz



Φ_N is the antisymetrized product of geminals (**AGP**) (first introduced by Hurley et al. '53):

$$\Phi_N(\vec{R}) = \mathcal{A} \prod_{i=1}^{N/2} \Phi(\vec{r}_i^{\uparrow}, \vec{r}_i^{\downarrow}),$$

$\Phi(\vec{r}_i^{\uparrow}, \vec{r}_i^{\downarrow}) = \phi(\vec{r}_i^{\uparrow}, \vec{r}_i^{\downarrow}) \frac{1}{\sqrt{2}} [|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle]$ (**geminal**) is a singlet and ϕ symmetric.

The AGP can be written as a *single determinant* of pairing orbitals

$$\Phi_N(\vec{R}) = \det(A_{ij}),$$

with $A_{ij} = \phi(\vec{r}_i^{\uparrow}, \vec{r}_j^{\downarrow})$

(and \vec{R} is the N -electron vector of coordinates).

Basis set dependence



The basis set expansion of the pairing function will determine the **rank** (number of non zero eigenvalues) of the matrix A_{ij}

- **Minimal** basis set: number of orbitals = $N/2$
rank of $A = N/2$
AGP = **HF** (best wave function written as a **single Slater** determinant)
- Expansion of the pairing **beyond** the minimal basis set: a **single AGP determinant** can be formally written as a *linear combination of many* Slater determinants (**resonance**)
- Correlation is introduced with the computational cost of a single determinant!!

General case



N electrons with N_{\uparrow} up spins (N_{\downarrow} down spins), $N_{\uparrow} \geq N_{\downarrow}$. We describe a pure spin state with total spin $S = |N_{\uparrow} - N_{\downarrow}|/2$ and maximum spin projection $S_z^{tot} = S$ by means of the antisymmetrized product of N_{\downarrow} singlet pairs and $2S$ unpaired orbitals

$$\Phi_N(\vec{R}) = \mathcal{A} \prod_{i=1}^{N_{\downarrow}} \phi(\vec{r}_i^{\uparrow}, \vec{r}_i^{\downarrow}) \prod_{j=N_{\downarrow}+1}^{N_{\uparrow}} \phi_j(\vec{r}_j^{\uparrow})$$

Applications:

- **atoms**: Casula et al., J. Chem. Phys. **119**, 6500 (2003)
- **molecules**: Casula et al., J. Chem. Phys. **121** 7110 (2004)
- **aromatic compounds**: Sorella et al, J. Chem. Phys. **127**, 014105 (2007)

Jastrow factor



(Sorella et al., 2007)

$$J(\vec{R}) = J_1(R)J_2(R)J_3(R)J_4(R)$$

One-body Jastrow:

$$J_1 = \exp \left[\sum_{ia} -(2Z_a)^{3/4} u(Z_a^{1/4} r_{ia}) + \sum_{ial} g_l^a \chi_{al}^J(\vec{r}_i) \right];$$

two-body Jastrow:

$$J_2 = \exp \left[\sum_{i<j} u(r_{ij}) \right],$$

i, j electron indexes, χ_{al}^J single part. orbit. of type l centered on nucleus a ;

r_{ia} and r_{ij} electron-ion and electron-electron distances.

$u(r) = F[1 - \exp(-r/F)]/2$ fixes the cusp conditions.

g_l^a and F are optimizable variational parameters.

Three and four-body Jastrow:

$$J_3, J_4(\vec{R}) = \exp \left(\sum_{i < j} f(\vec{r}_i, \vec{r}_j) \right),$$

\vec{r}_i the nucleus-ion distance, $f(\vec{r}_i, \vec{r}_j) = \sum_{ablm} g_{lm}^{ab} \chi_{al}^J(\vec{r}_i) \chi_{bm}^J(\vec{r}_j)$, and g_{lm}^{ab} optimizable parameter.

- J fixes the cusps, takes into account weak electron-electron interactions of the vdW type, and suppresses higher energy configurations with overlapping valence bonds.

Molecular orbital expansion



$$\phi(\vec{r}, \vec{r}') = \sum_{j=1}^{n-2S} \lambda_j \phi_j(\vec{r}) \phi_j(\vec{r}'),$$

n is large enough, and $\{\phi_j\}$ is an orthogonal single particle basis set (**molecular orbitals** (MOs)), which reaches its complete basis set limit (CBS) for $n \rightarrow \infty$.

$\phi_i(\vec{r}) = \sum_{a,j} \zeta_{a,j}^i \varphi_{a,j}(\vec{r})$, $\varphi_{a,j}$ atomic orbital of type j centered on atom a .

$\zeta_{a,j}^i$ and λ_j variational parameters.

Minimization of the wave function



To find better nodes, one has to optimize a variational wave functions which has several parameters.

- Stochastic Reconfiguration: S. Sorella, Phys. Rev. B **71**, 241103 (2005).
- Stochastic reconfiguration with Hessian acceleration: C. J. Umrigar, J. Toulouse, C. Filippi, S. Sorella, and R. G. Hennig, PRL **98**, 110201 (2006).

Binding energy



- **Atoms** are well described by a correlated Hartree-Fock (**JHF**) (Jastrow applied to Hartree-Fock Slater determinant provides at least $\sim 90\%$ of the correlation energy within the DMC)
- **Idea:** extend JHF approximation for the chemical bond, by using a RVB wavefunction with an *appropriate* number of **molecular orbitals** n^* in the pairing function. n^* univocally determined by requiring to obtain JHF energy when atoms are at large distance.
- **Ansatz:** $B = E(\text{molecule}, n^*) - 2 E(\text{atom}, JHF)$ (homonuclear dimers)!

Constrained variational minimization



Molecule composed of atoms A_i :

$$n_{HF} \leq n^* \leq \tilde{n} (= \sum_i N_{\uparrow}(A_i))$$

JAGP n^* wave function

If $n^* = n_{HF}$, then **JAGP** n^* reduces to a **JHF** description of the molecule (e.g. Be_2 , B_2).

- Optimization with **rank** of the AGP *fixed* to equal n^* !!!

Be₂: a challenging molecule!(I)



Recent review on experimental and computational studies for Be₂, with new experimental reference data (Merrit et al, *sciencexpress*, may 2009)

- 1930: experiments \Rightarrow ground state interaction between two Be atoms is repulsive. Also confirmed by SCF calculations and some CI studies.
- Then shallow van der Waals minimum ($R_e \sim 8 \div 9a_0$)/deeper minima at shorter bond lengths ($R_e \sim 4.5a_0$)
- Technical challenge for experimental studies:
 1. high melting and boiling points and almost monoatomic vapour
 2. Be is easily oxidized and the oxide is toxic.



- Improvements in experimental techniques (pulsed laser ablation): gas phase spectra
- Results: shallow minimum but shorter bond length ($R_e \sim 4.6a_0$)
- Consequence: new input in computational studies
- Casula et al (2004): fail to find the bond at the expected distance

Be₂: a challenging molecule!(II)



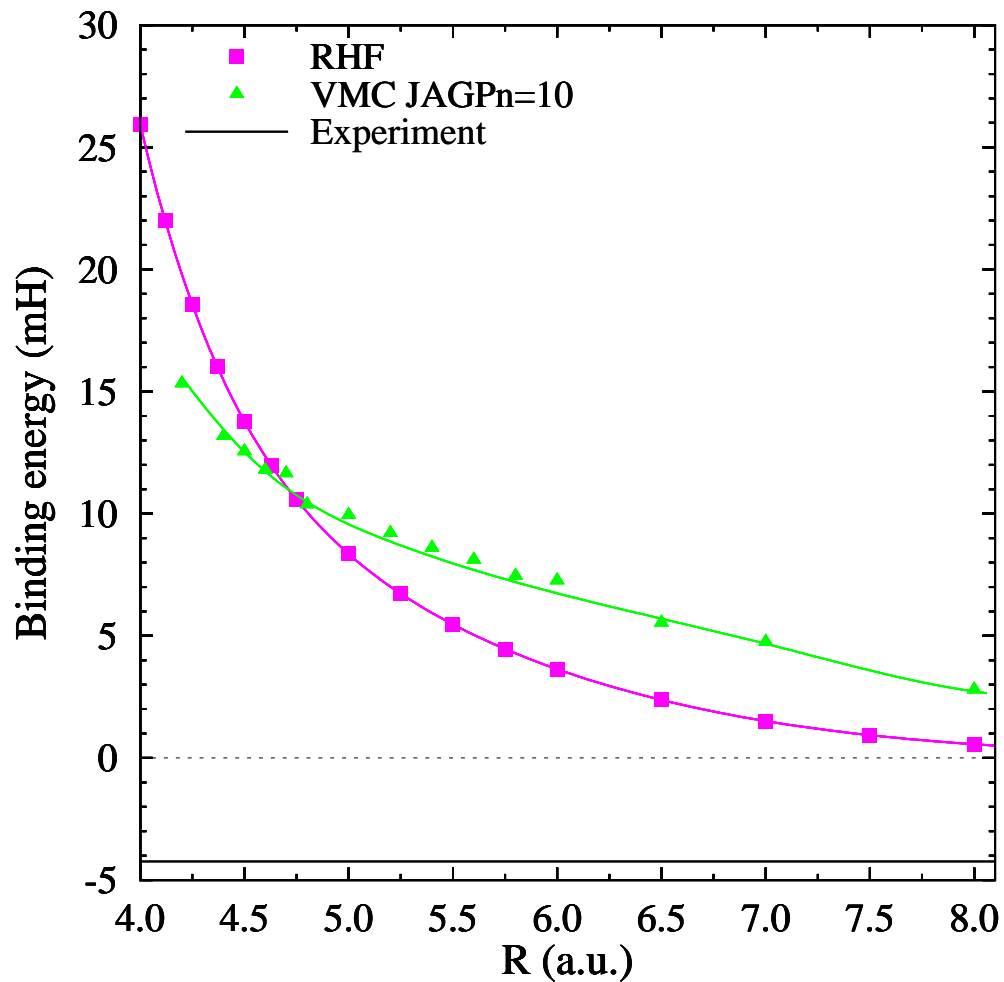
Present QMC approach:

$$n^* = n_{HF} = 4$$

Hence JHF description of the molecule through the constrained optimization of the JAGPn* wave function and JHF description of the fragments in the atomization limit!

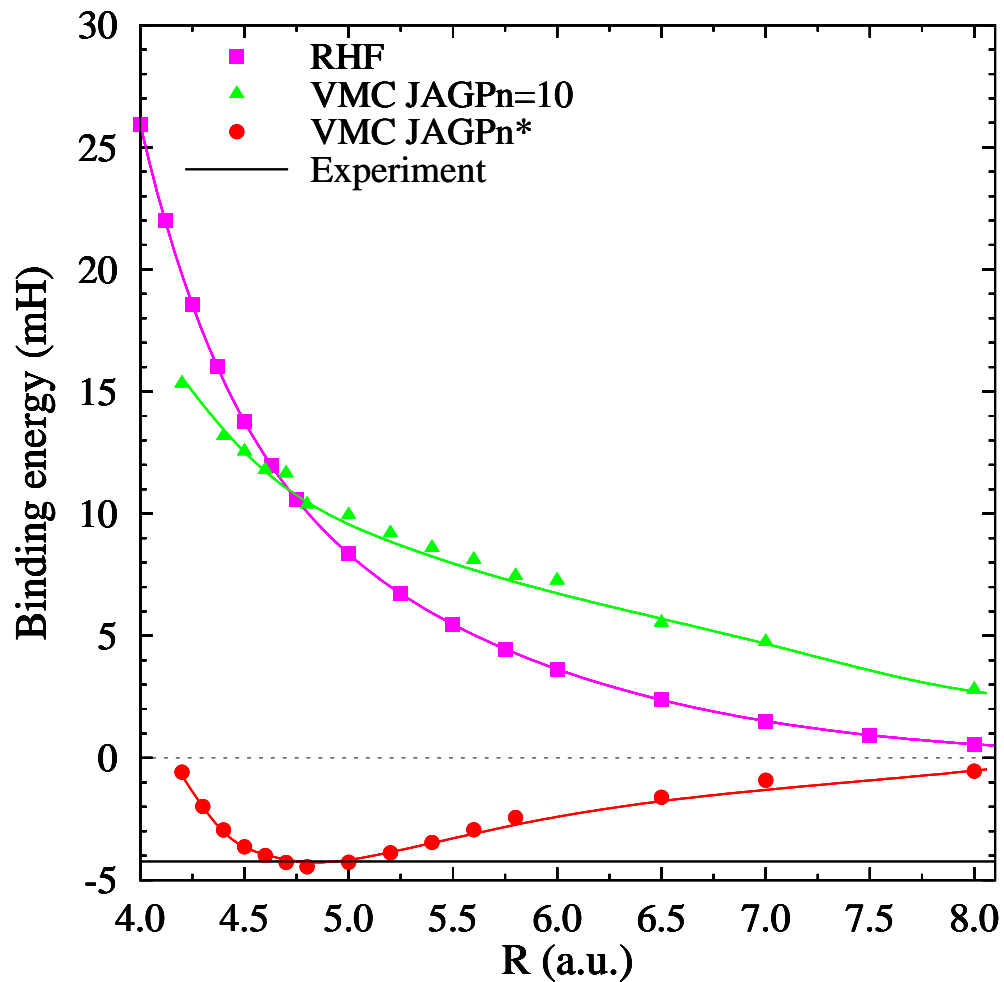
- All electron calculations
- $6s4p2d$ uncontracted Slater basis set for the AGP, $4s4p$ for J

Be₂: a challenging molecule!(III)

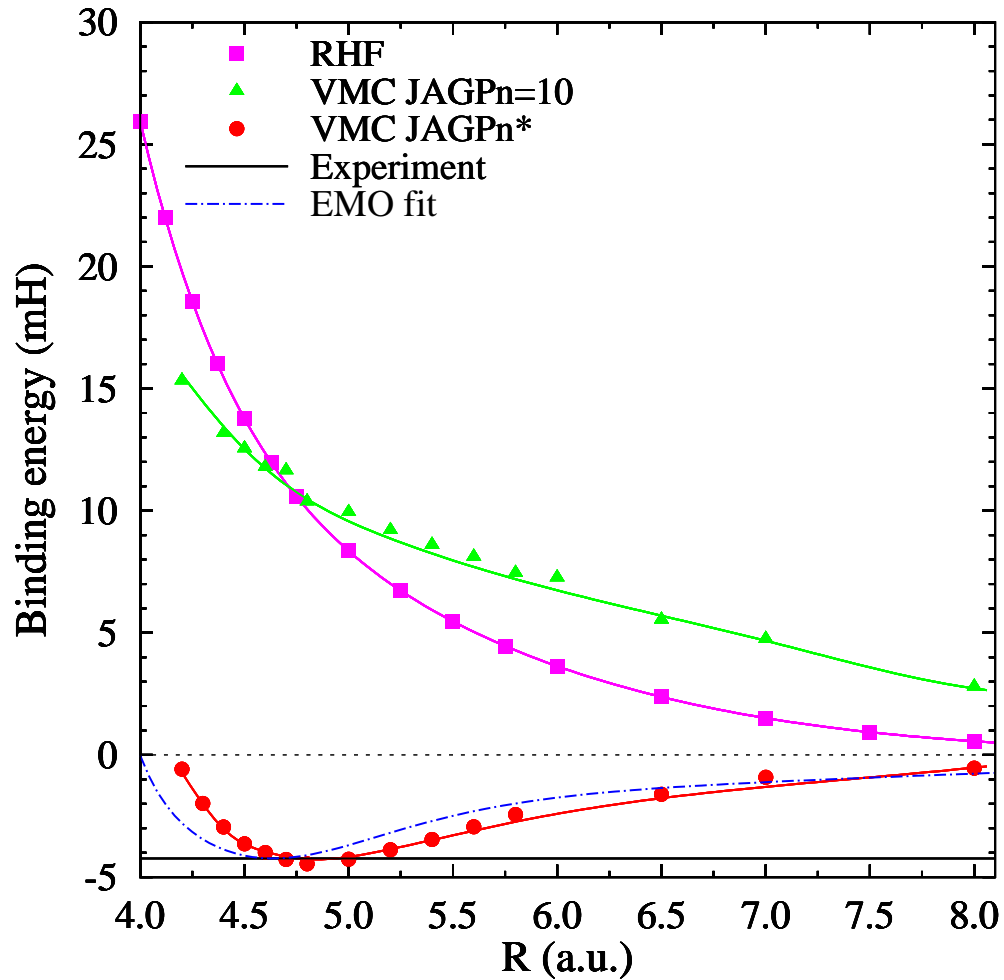


RHF by Roeggen et al. (1996)

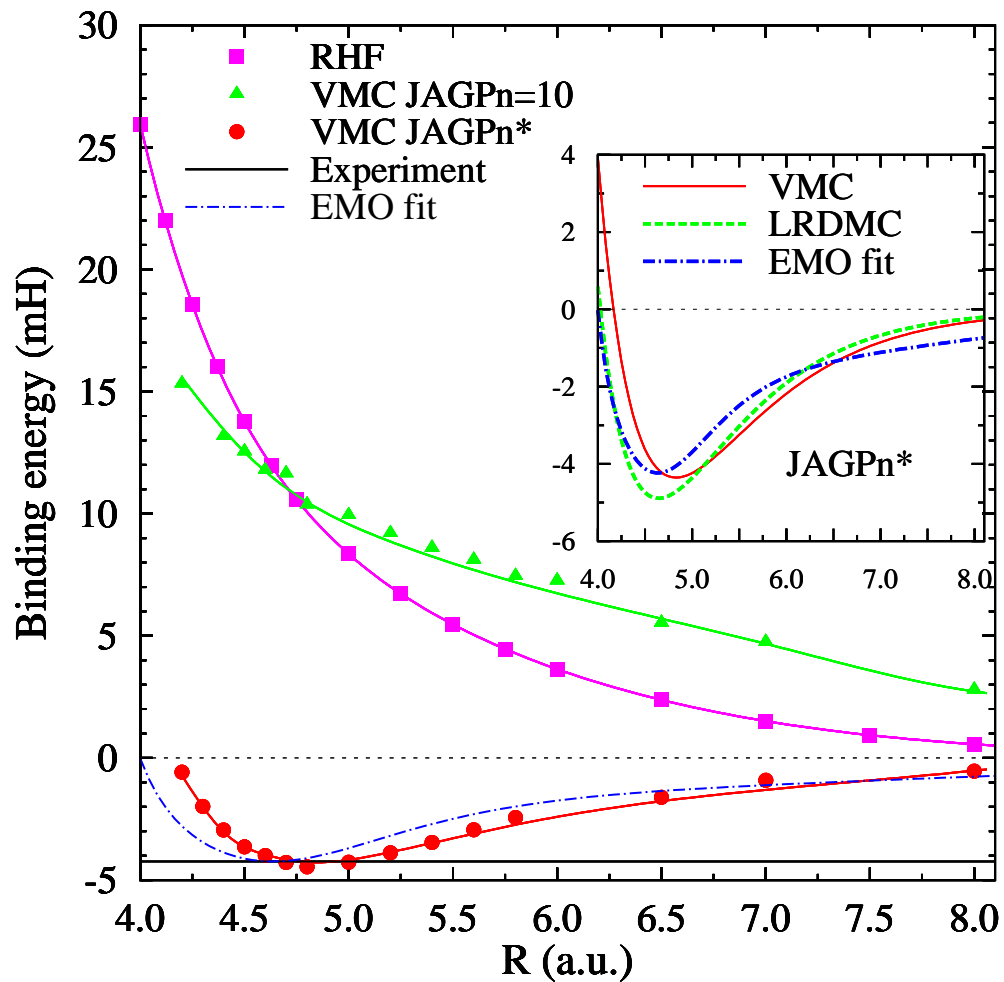
Be₂: a challenging molecule!(III)



Be₂: a challenging molecule!(III)

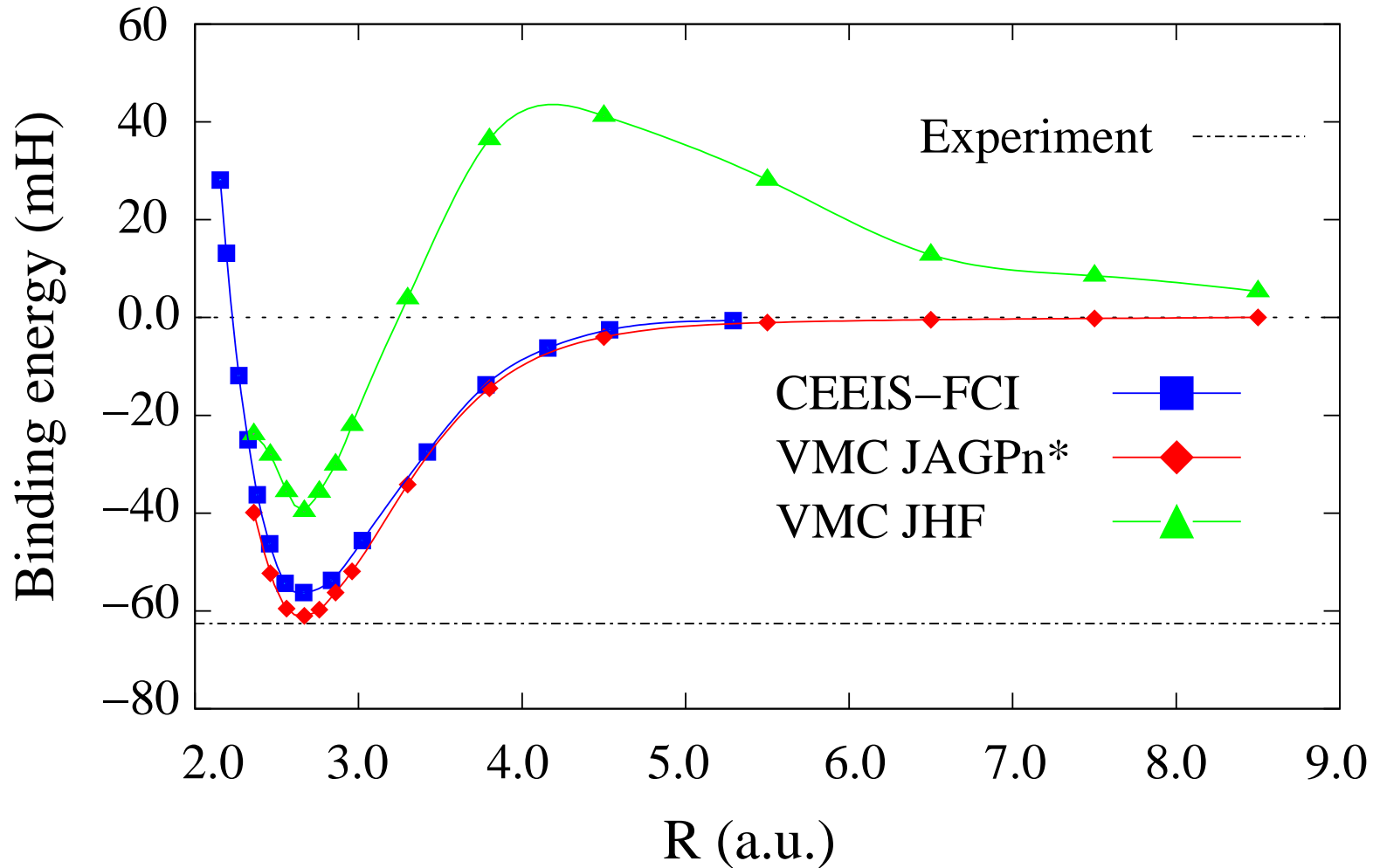


Be₂: a challenging molecule!(III)





$$n^* = n_{HF} + 1$$



CEEIS-FCI by Bytautas et al, 2007

Results for diatomic molecules



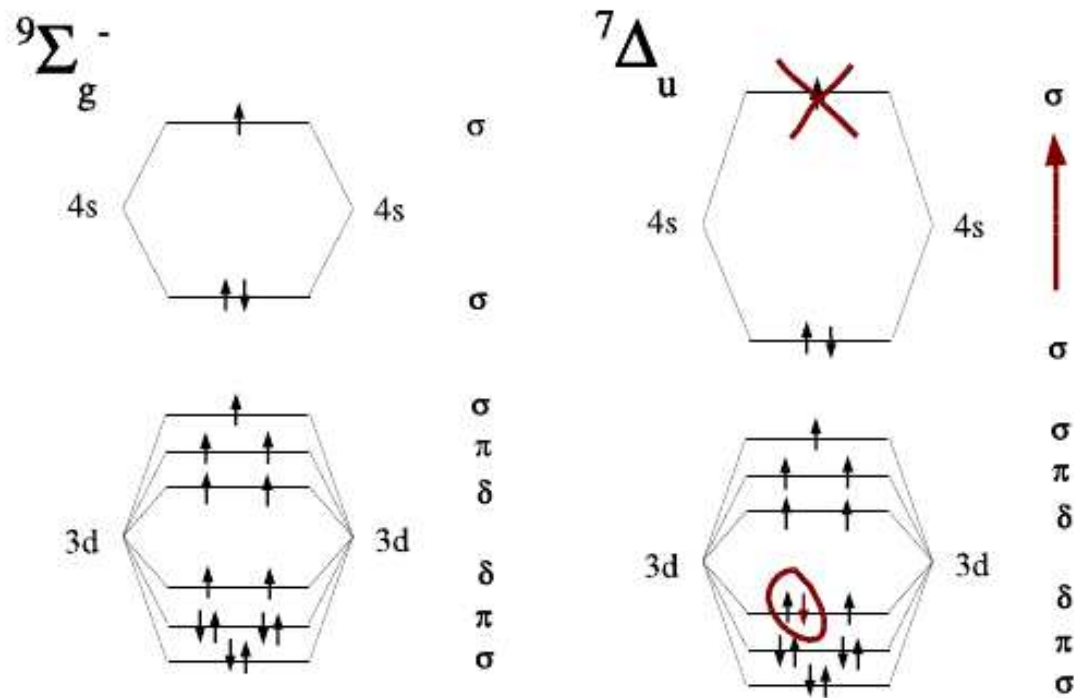
<i>Bond length (a.u.)</i>								
	Be ₂ (all el.)	B ₂	C ₂	N ₂	O ₂	F ₂	LiF	CN
JHF VMC	4.85(5)	3.041(6)	2.367(2)	2.048(1)	2.27(1)	2.66(1)	2.95(4)	2.185(6)
JAGPn* VMC	=	=	2.334(6)	2.075(2)	2.268(7)	2.661(5)	2.92(2)	2.200(6)
JHF LRDMC	4.65(7)	3.021(9)	2.369(3)	2.051(1)	2.270(4)	2.665(9)	2.949(8)	2.201(3)
JAGPn* LRDMC	=	=	2.337(6)	2.075(1)	2.277(4)	2.663(3)	2.950(7)	2.202(2)
Exact estim.	4.63 ^a	3.005 ^c	2.3481 ^b	2.075 ^c	2.283 ^c	2.668 ^c	2.955 ^c	2.214 ^c
<i>Well depth (eV)</i>								
	Be ₂ (all. el)	B ₂	C ₂	N ₂	O ₂	F ₂	LiF	CN
JHF VMC	0.120(5)	2.754(3)	5.538(9)	9.662(3)	4.976(8)	1.124(4)	5.93(2)	7.52(1)
JAGPn* VMC	=	=	6.327(9)	9.874(2)	5.060(7)	1.671(2)	5.96(2)	7.68(1)
J×SD DMC	0.125(1)	2.798(3)	5.656(3)	9.583(3)	4.992(7)	1.349(6)	–	–
JHF LRDMC	0.143(6)	2.797(2)	5.763(9)	9.665(2)	5.070(5)	1.452(3)	6.049(6)	7.661(5)
JAGPn* LRDMC	=	=	6.297(8)	9.882(1)	5.126(5)	1.686(2)	6.056(6)	7.744(5)
Exact estim.	0.1153(3) ^a	2.91(6) ^d	6.44(2) ^e	9.908(3) ^e	5.241(3) ^e	1.693(5) ^e	6.02(9) ^f	7.85(9) ^f
<i>ZPE (mH)</i>								
	Be ₂ (all el.)	B ₂	C ₂	N ₂	O ₂	F ₂	LiF	CN
JHF VMC	0.56(5)	2.49(5)	4.3(1)	6.38(6)	3.8(1)	2.20(3)	2.3(2)	4.9(1)
JAGPn* VMC	=	=	4.2(1)	5.48(3)	3.85(9)	2.20(3)	2.1(2)	4.87(8)
JHF LRDMC	0.61(9)	2.51(7)	4.38(3)	5.83(6)	3.77(5)	2.16(3)	2.18(8)	4.81(3)
JAGPn* LRDMC	=	=	4.3(1)	5.51(2)	3.70(9)	2.22(2)	2.10(6)	4.82(4)
Exp.	0.56 ^a	2.4 ^c	4.2 ^e	5.4 ^e	3.6 ^e	2.1 ^e	2.07 ^c	4.71 ^c

Fe₂ (Intro)



Transition metal compounds presents:

- strong electron correlations in the nearly half-filled *d* orbitals
- non trivial ordering of low-lying energy states which differ by their spin



Fe₂: Former theoretical studies



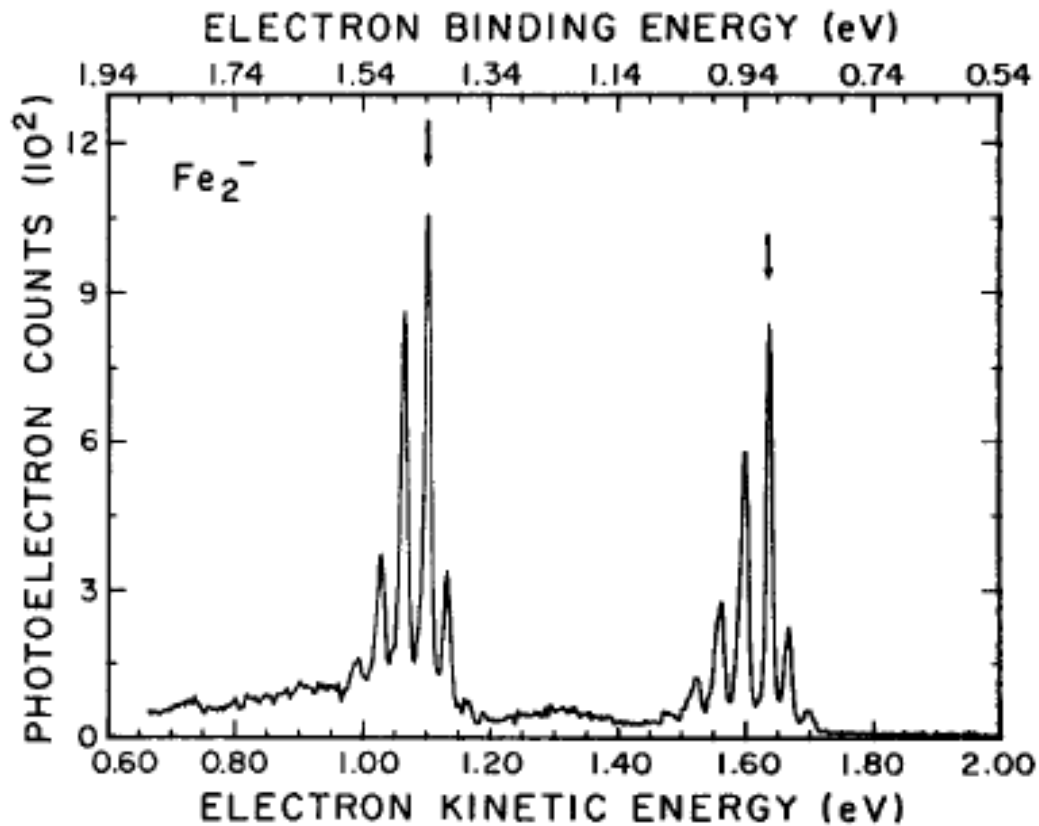
- ${}^7\Delta_u$: **DFT** studies with various functionals (Salahub and coworkers (1993,1994,2002), Bauschlicher and Co. (2003)) + **MRCI** calculations (Tatewaki et al., 1988)
- ${}^9\Sigma_u^-$: recent **MRCI** (Hübner et al, 2002) + **DFT** studies with CC (Irigoras et al., 2003) and $+U$ corrections (Kulik et al., 2006)
- **VMC** energy of ${}^9\Sigma_u^-$ and ${}^7\Delta_u$ are close to each other (Casula, PhD thesis)

Fe₂: Experiments (I)



Negative-ion photoelectron spectroscopy (PES) (Leopold et al. 1986,1988):

Fe₂⁻ excited by incoming photon



Peaks have *same* ω_e and R_e !!

Explanation: Fe₂⁻ ground state is $^8\Sigma_u^-$ and peaks correspond to $^9\Sigma_g^-$ (ground state) and $^7\Sigma_g^-$ (excited state) of Fe₂ (due to detachment of 4s-like MOs and strongly bonding character of $\sigma_g(4s)$)!

Fe₂: Experiments (II)



Electron spin resonance (ESR) (Baumann et al. 1984):

They fail to observe Fe₂. Thus, Fe₂ *ground state* cannot be ${}^9\Sigma_g$, unless Fe₂ has a magnetic split $> 8 \text{ cm}^{-1}$ which would provide an energy split not detectable by experim. setup.

Fe₂: our QMC description (I)



- Fe₂: ${}^9\Sigma_g^-, {}^7\Sigma_g^-, {}^7\Delta_u$
- Fe₂⁻: ${}^8\Sigma_u^-, {}^8\Delta_g$
- Neon-core pseudopotential (Dolg et al., 1987)
- [8s5p6d/2s1p1d] contracted Gaussian basis set (convergence in energy differences for atomic calculations checked with 8s5p6d3f basis)
- Jastrow basis set 4s3p2d
- ${}^9\Sigma_g^-, {}^8\Sigma_u^-,$ and ${}^8\Delta_g$: $n^* = N_{\uparrow} \Rightarrow$ JHF wave function!
- ${}^7\Delta_u$ and ${}^7\Sigma_g^-$: $n^* = N_{\uparrow} + 1 \Rightarrow$ JAGPn* wave function!

Fe₂: our QMC description (II)



Controlled dissociation

- Some symmetries may be lost in the dissociation
- For Fe₂: total angular momentum conserved for rotations around molecular axis, thus fragments may not have definite total angular momentum
- Correction has to be applied to the atomic reference (given by the energy difference between hybrid JHF atomic fragment reached upon stretching JAGP n^* and fully symmetric JHF atomic state (with same primitive basis))



Dissociation limits of various Fe₂ states for the RVB wave function

Fe ₂ state	from our wf	exact
${}^7\Sigma_g^- \rightarrow$	${}^5D + {}^5[1]$	${}^5D + {}^5F$
${}^9\Sigma_g^- \rightarrow$	${}^5D + {}^5[0]$	${}^5D + {}^5F$
${}^7\Delta_u \rightarrow$	${}^5D + {}^5[0]$	${}^5D + {}^5D$
${}^8\Delta_g \rightarrow$	${}^5D + {}^4[0]$	${}^5D + {}^4F$
${}^8\Sigma_u^- \rightarrow$	${}^5D + {}^4[0]$	${}^5D + {}^4F$

Fe₂: our QMC description (III)



Calculations for the Fe atom

	LRDMC	exp.
5D	-123.7819(11)	
5F	-123.7520(11)	
$^5[0]$	-123.73986(72)	
$^5[1]$	-123.71856(75)	
4F	-123.77731(94)	
$^4[0]$	-123.76544(81)	
$^5D \rightarrow ^5F$ (eV)	0.81(4)	0.87 (a)
$^4F \rightarrow ^5D$ (eV)	-0.12(4)	0.15 (a)

(a) Moore et al. (1949)

Fe₂: LRDMC energies



	Energy (Hartree)	R_e (a.u.)	ω_e (cm^{-1})	exp ω_e (cm^{-1})
${}^9\Sigma_g^-$	-247.5486(20)	4.093(19)	301(15)	299.6 (a)
${}^7\Sigma_g^-$	-247.5036(20)	4.081(18)	327(15)	300(15) (b)
${}^7\Delta_u$	-247.5351(30)	3.894(18)	373(32)	-
${}^8\Delta_g$	-247.5585(30)	3.908(14)	354(24)	-
${}^8\Sigma_u^-$	-247.5706(42)	4.276(28)	210(20)	250(20) (b)

(a) Moskovits (1980) (b) Leopold (1986)

- ${}^9\Sigma_g^-$, ${}^7\Sigma_g^-$, and ${}^8\Sigma_u^-$ in agreement with PES experiment (ω_e and bond elongation)!
- ${}^7\Delta_u$ ω_e in agreement with DFT (Sahalub, 2002; Bauschlicher, 2003)

⇒ Confirmation of peak symmetries in PES!

Fe₂: Asymptotic limit corrections



	Energy (Hartree)	Corrected (Hartree)	Difference (eV)	Exp (eV)
${}^7\Sigma_g^-$	-247.5036(20)	-247.5370(24)	+0.64(7)	+0.534(4) (a)
${}^9\Sigma_g^-$	-247.5486(20)	-247.5608(24)	0.0	
${}^7\Delta_u$	-247.5351(30)	-247.5771(33)	-0.44(9)	-
${}^8\Delta_g$	-247.5585(30)	-247.5703(33)	-0.26(9)	-
${}^8\Sigma_u^-$	-247.5706(42)	-247.5824(44)	-0.59(12)	-0.902(8) (a)

(a) Leopold et al., 1986

- After the correction ${}^7\Delta_u$ is the **ground state!**
- Experimental $R_e = 3.82(4)$ (Purdum et al., 1982)

Conclusions and References



- Cheap method for studying molecules within chemical accuracy
- Single determinant method
- Importance of the optimization
- Answer to the controversial issue of Fe₂ ground state
- **First row dimers:** M. Marchi et al., arXiv:0907.1390/cond-mat.mtr.sci
- **Iron dimer:** M. Casula et al., arXiv:0906.4824/cond-mat.other
(accepted for publication by Chem. Phys. Lett.)

JHF atomic correlation energy



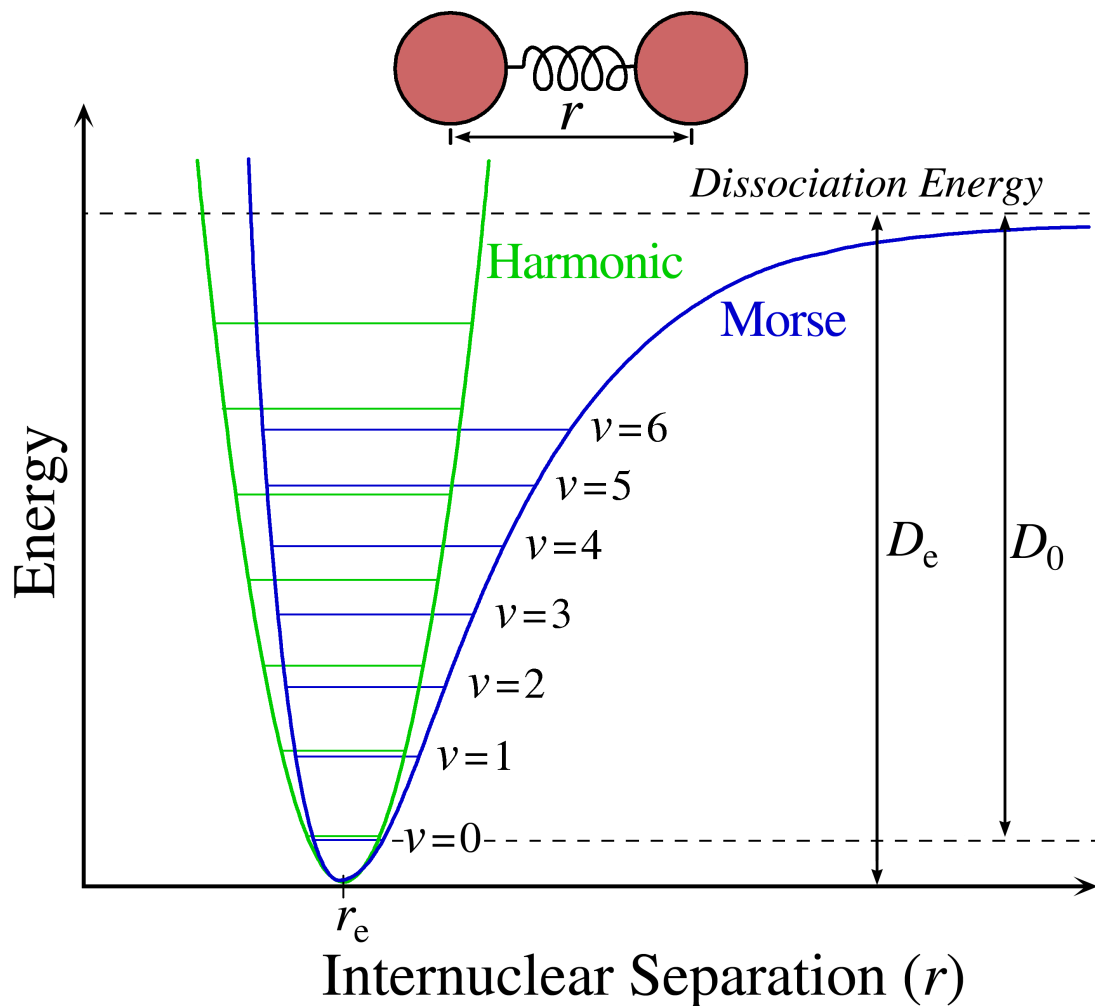
Atom	RHF	Est. exact	JHF VMC	JHF LRDMC	%
Li	-7.432727 ^a	-7.47806 ^a	-7.47707(6)	-7.47807(3)	100%
Be	-14.573023 ^a	-14.66736 ^a	-14.64747(9)	-14.6575(1)	89.5%
B	-2.54375616 ^b	-2.61940948 ^b	-2.6031(1)	-2.6110(1)	88.9%
C	-5.32903005 ^b	-5.43249352 ^b	-5.4105(1)	-5.4216(1)	89.5%
N	-9.66837630 ^b	-9.79973109 ^b	-9.7771(3)	-9.7898(1)	92.4%
O	-15.70844748 ^b	-15.90165954 ^b	-15.8754(1)	-15.89233(8)	95.2%
F	-23.93849161 ^b	-24.19290003 ^b	-24.1683(4)	-24.1855(2)	97.09%

MO constrained optimization



1. Compute unconstrained derivatives D such that $D = U_T V$ (dimension $L \times N/2$).
2. Constrain the derivatives D via projectors written in terms of the current MOs.
3. Optimize the unconstrained λ coefficients with usual techniques. Do the projection and apply singular value decomposition. Thus we get the new MOs.
4. Go to step 1 until convergence in the energy is reached.

Morse potential fit (I)



Morse potential fit (II)



- $V(r) = D_e [1 - e^{-a(r-R_e)}]^2$

- $ZPE = \frac{1}{2} \hbar \omega_0,$

- $\omega_0 = a \sqrt{\frac{2D_e}{\mu}}$

Expanded Morse Oscillator (EMO)



Merrit et al., scienceexpress (2009)

$$V(r) = D_e [1 - e^{-\phi(r)(r-R_e)}]^2$$

$$\phi(r) = \sum_{i=0}^5 \phi_i \left(\frac{r^p - r_{ref}^p}{r^p + r_{ref}^p} \right),$$

$$p = 4, r_{ref} = 2.45 \text{ \AA}.$$

They find $D_e = 929.7(2.0) \text{ cm}^{-1} \simeq 0.1153(3) \text{ eV}$

Lattice regularized DMC (LRDMC)



- Computational effort increases with atomic charge Z
- **Non local pseudopotentials** to replace valence core electrons
- To perform DMC one has to use a **locality approximation** to rewrite the pseudopotential. But the E_{FN} of the *true* Hamiltonian is not any more accessible
- **LRDMC**: lattice regularization of H allows to use pseudopotential in a variational consistent framework!! (Casula et al, PRL 95, 100201 (2005))