

Precision calculations for precision measurements: a quantum chemist's point of view

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Motto

Ted Hänsch, Nobel lecture “Passion for precision”

“In our highly complex and ever changing world it is reassuring to know that certain physical quantities can be measured and predicted with very high precision. Precision measurements have always appealed to me as one of the most beautiful aspects of physics. With better measuring tools, one can look where no one has looked before. More than once, seemingly minute differences between measurement and theory have led to major advances in fundamental knowledge. The birth of modern science itself is intimately linked to the art of accurate measurements (add. RM and precision calculations).”

Plan of the talk

- ★ Motivation
- ★ Theoretical model for precision calculations: state-of-the-art
- ★ Challenges for theoreticians and experimentalists
- ★ Examples
 - dissociation energy and scattering length of the ground state hydrogen molecule
 - preliminary results for the $a^3\Sigma_u^+$ of Li_2
 - theoretical predictions for the $A^1\Sigma_u^+ + c^3\Pi_u$ manifold of Sr_2

Theoretical motivation

- ★ Limit of the present day predictive power of the quantum theory

- ★ Open questions in molecular physics
 - molecular gerade/ungerade mixing
 - finite nuclear size corrections
 - QED at the α^4 level
 - evidence for the QED retardation in the spectra
 - long-range nuclear forces

- ★ Beyond the standard model
 - time variation of the electron to proton mass ratio
 - time variation of the fine structure constant
 - electron dipole moment
 - mass of the neutrino

Włodzimierz Kołos



Schrödinger-Coulomb equation for N particles

$$\left(-\frac{1}{2} \sum_{i=1}^N \frac{\nabla_i^2}{m_i} + \sum_{i<j}^N \frac{Z_i Z_j}{r_{ij}} \right) \Psi = E \Psi$$

where (in atomic units) $Z_i = -1$ and $m_i = 1$ when i labels an electron.

The Schrödinger-Coulomb equation:

- ★ is mathematically well understood (self-adjoint operator on the left)
- ★ with a very small number of “material parameters” (Z_i 's and m_i 's) it has an enormous predictive power. Predicts e.g:
 - photochemistry of organic molecules
 - rovibrational spectra of millions of molecules
 - rates of millions of chemical reactions
- ★ forms a basis for a perturbative inclusion of fine, hyperfine, quantum field theory (QED), and nuclear structure effects

Nonrelativistic theory (Schrödinger-Coulomb equation)

Born-Oppenheimer energy	36112.5927(1)
Adiabatic correction	5.7711(1)
Nonadiabatic correction	0.4339(2)
Total nonrelativistic	36118.7978(2)
Experiment	36118.0696(4)
Missing (relativity?) effects	-0.7282(4)

Relativity: the Dirac-Coulomb equation

This is a naive generalization of the Schrödinger equation obtained by adding the Coulombic interelectronic repulsion to the sum of one-electron Dirac Hamiltonians $\hat{h}_D = c\vec{\alpha}\vec{p} + \beta mc^2$

$$\hat{H}_{DC} = \sum_i^N \hat{h}_D(i) + \sum_{j<j}^N \frac{1}{r_{ij}}$$

This equation forms a basis for the relativistic quantum chemistry but is rejected by many physicists because of the following pathologies:

- ★ \hat{H}_{DC} has only a continuous spectrum from $-\infty$ to ∞ (no bound states).
- ★ Physical states are modeled by Feshbach-type resonances with an unphysical width of the order of $Z^3\alpha^3$ (Pestka et al., JPB 2006, 2007)
- ★ Ground state is unstable and has a finite lifetime
- ★ Elimination of the width by Feshbach projection (Sucher) is not unique
- ★ Wrong mass dependence of the relativistic correction even for the hydrogen atom (wrong coefficient at the $\alpha^2 m_e/m_p$ term)

Further problems with the Dirac-Coulomb equation

- ★ Since \hat{H}_{DC} has no square integrable (L^2) eigenfunctions there are problems with the probabilistic interpretation of its eigenfunctions
- ★ When L^2 techniques are used to solve the DC equations the energies become fuzzy and can be determined only with an accuracy of the order of $Z^3\alpha^3$. How to add QED corrections to so imprecisely defined energies?
- ★ For real, physical autoionizing states it is not clear how to separate the physical width from the unphysical one.

“The Dirac-Coulomb equation is a mathematical and physical nonsense”

Werner Kutzelnigg, Mariapfarr Workshop, February 2011

In fact, the DC Hamiltonian is mathematically well defined and makes a very useful model if interpreted correctly.

Problems arise only when one wants to solve it with a very high accuracy and improve on it by adding QED corrections.

Bound state QED: a quantum chemist view

The QED Hamiltonian has the form

$$\hat{H} = \hat{H}_\gamma + \hat{H}_e + \hat{H}_{\text{int}}$$

where \hat{H}_γ and \hat{H}_e are Hamiltonians for noninteracting photons (created by $c_{k\lambda}^\dagger$), electrons (created by a_s^\dagger), and positrons (created by b_p^\dagger):

$$\hat{H}_\gamma = \sum_{k,\lambda} \hbar |k| c_{k\lambda}^\dagger c_{k\lambda} \quad \hat{H}_e = \sum_s \epsilon_s a_s^\dagger a_s + \sum_p \epsilon_p b_p^\dagger b_p$$

and \hat{H}_{int} takes care of their interaction:

$$\hat{H}_{\text{int}} = - \int j_\mu(r) A_\mu(r) d^3r$$

The vector potential $A_\mu(r)$ is a linear form of $c_{k\lambda}^\dagger$ and $c_{k\lambda}$ and the current operator $j_\mu(r)$ is a quadratic form of a_s^\dagger , a_s , b_p^\dagger , and b_p .

The QED Hamiltonian is physically sound but, unfortunately, it lacks a rigorous mathematical sense. It can be used only in perturbation theory, either in the high- Z or the low- Z regime.

Intermediate values of Z still present a challenge

Nonrelativistic QED

In nonrelativistic QED the energy of a quantum system is expanded in powers of the fine-structure constant α

$$E = E^{(0)} + \alpha^2 E^{(2)} + \alpha^3 E^{(3)} + \alpha^4 E^{(4)} + \dots,$$

where $E^{(0)}$ is the nonrelativistic energy, and $E^{(k)}$ are expressed in terms of expectation values of certain operators with nonrelativistic wave functions (i.e., obtained from the Schrödinger equation), or in terms of nonrelativistic response functions. For instance

$$\alpha^2 E^{(2)} = \langle H_{\text{BP}} \rangle = \langle H_{\text{mv}} \rangle + \langle H_{\text{D1}} \rangle + \langle H_{\text{D2}} \rangle + \langle H_{\text{OO}} \rangle + \langle H_{\text{SO}} \rangle + \langle H_{\text{SS}} \rangle$$

where H_{BP} is the complete Breit-Pauli Hamiltonian including electron-nucleus terms proportional to $\alpha^2(m_e/m_p)^n$, $n=1,2,3$ (so called recoil terms).

When the recoil terms are neglected and the adiabatic wave functions are used to compute expectation values, the $\alpha^k E^{(k)}$ corrections can be expressed as radial expectation values of the relativistic interatomic potentials:

$$V_{\text{int}}(R) = V_0(R) + \alpha^2 V_2(R) + \alpha^3 V_3(R) + \alpha^4 V_4(R) + \dots$$

α^3 QED Correction

When recoil effects of the order of $\alpha^3(m_e/m_p)^n$ are neglected the $\alpha^3 E^{(3)}$ QED corrections is

$$\alpha^3 \frac{16}{3} \left(\frac{19}{30} - 2 \ln \alpha - \ln K \right) \langle \delta(\mathbf{r}_{1a}) \rangle + \alpha^3 \left(\frac{164}{15} + \frac{14}{3} \ln \alpha \right) \langle \delta(\mathbf{r}_{12}) \rangle - \alpha^3 \frac{7}{6\pi} \langle P(r_{12}^{-3}) \rangle$$

where $P(r_{12}^{-3})$ is a distribution defined by

$$\langle \psi | P(r_{12}^{-3}) | \psi \rangle = \lim_{a \rightarrow 0} \langle \psi | \theta(r_{12} - a) r_{12}^{-3} + 4\pi (\gamma + \ln a) \delta(\mathbf{r}_{12}) | \psi \rangle,$$

and $\ln K$ is the infamous Bethe logarithm (in full nonadiabatic form)

$$\ln K = \frac{\langle \psi | \mathbf{j} (\hat{H} - E^{(0)}) \ln [(\hat{H} - E^{(0)}) / \text{Ry}_\infty] \mathbf{j} \psi \rangle}{\langle \psi | \mathbf{j} (\hat{H} - E^{(0)}) \mathbf{j} \psi \rangle}.$$

$\mathbf{j} = -\mathbf{p}_1/m_e - \mathbf{p}_2/m_e + \mathbf{p}_a/m_p + \mathbf{p}_b/m_p$ is the electric current operator. An adiabatic approximation to $\ln K$ is defined as

$$\ln K^{\text{ad}} = \frac{\langle \ln K^{\text{el}}(R) D_1(R) \rangle}{\langle D_1(R) \rangle}$$

where $D_1(R) = \langle \delta(\mathbf{r}_{1a}) \rangle_{\text{el}}$ and $\ln K^{\text{el}}(R)$ is the electronic Bethe logarithm.

How does it work: dissociation energies of H_2 and D_2

		H_2	D_2
α^0	Nonrelativistic	36118.7978(2)	36749.0910(2)
α^2	Mass-velocity	4.4273(2)	4.5125(2)
	1-el. Darwin	-4.9082(2)	-4.9873(2)
	2-el. Darwin	-0.5932(1)	-0.5993(1)
	Breit	0.5422(1)	0.5465(1)
	Total α^2	-0.5319(3)	-0.5276(3)
$\alpha^2 m_e/m_p$	Estimate	0.0000(4)	0.0000(2)
α^3	1-el. Lamb shift	-0.2241(1)	-0.2278(1)
	2-el. Lamb shift	0.0166(1)	0.0167(1)
	Araki-Sucher	0.0127(1)	0.0128(1)
	Total α^3	-0.1948(2)	-0.1983(2)
$\alpha^3 m_e/m_p$	Estimate	0.0000(2)	0.0000(1)
α^4	One-loop term	-0.0016(8)	-0.0016(8)
Total theory	Jeziorski and coll. 2009	36118.0695(10)	36748.3633(9)
Expt.	Eyler, 2004	36118.062(10)	36748.343(10)
Expt.	Merkt&Ubachs, 2009/10	36118.0696(4)	36748.36286(68)

QED retardation in the long-range

The standard derivation of the Casimir-Polder formula utilizes the nonrelativistic QED. The Hamiltonian is composed of a sum of the nonrelativistic Hamiltonians for the monomers, the Hamiltonian of the quantum electromagnetic field, and the coupling between electrons, nuclei and the E-M field:

$$\mathcal{H} = H^A + H^B + H_{\text{E-M}} + H_{\text{int}}.$$

$$H_{\text{E-M}} = \int d^3\mathbf{r} \frac{1}{2} [\mathbf{E}^2(\mathbf{r}) + \mathbf{B}^2(\mathbf{r})] = \sum_{\lambda} \int d^3\mathbf{k} \omega_k a_{\mathbf{k}\lambda}^{\dagger} a_{\mathbf{k}\lambda},$$

and the interaction (in the simplest case of dipole coupling) is:

$$H_{\text{int}} = - \sum_a q_a \mathbf{r}_a \mathbf{E}(\mathbf{R}_A) - \sum_b q_b \mathbf{r}_b \mathbf{E}(\mathbf{R}_B).$$

Application of the perturbation theory to the Hamiltonian \mathcal{H} leads to the following expression for the dispersion energy:

$$E_{\text{disp}}^{(2)}(\text{ret}) = - \frac{1}{\pi R^6} \int_0^{\infty} \alpha_0^2(i\omega) \exp(-2\omega R/c) P(\omega R/c) d\omega,$$

$$P(x) = x^4 + 2x^3 + 5x^2 + 6x + 3.$$

QED retardation in the long-range

At very large distances the retarded dispersion energy shows an R^{-7} behavior:

$$E_{\text{disp}}^{(2)}(\text{ret}) \xrightarrow{R \gg \lambda_0} -\frac{23\alpha_0(0)\alpha_0(0)}{2\pi\alpha R^7}.$$

At small R it recovers the following terms of the relativistic potential:

$$E_{\text{disp}}^{(2)}(\text{ret}) \xrightarrow{R \ll \lambda_0} -\frac{C_6}{R^6} + \frac{C_6^{\text{CG}}\alpha^2 + C_6^{\text{QED}(3)}\alpha^3}{R^6} + \frac{C_4^{\text{BP}}\alpha^2}{R^4} + \frac{C_3^{\text{AS}}\alpha^3}{R^3} + \dots$$

The $\frac{(C_6^{\text{BP}} - C_6^{\text{CG}})\alpha^2}{R^6}$ and $\frac{C_5^{\text{AS}}\alpha^3}{R^5}$ not included in the retardation.

How does it work: long-range interactions and scattering length for H_2

Approximation	a	C_3	C_4	C_5	C_6	C_7
BO	0.4250				6.4990	
BO+AD	0.2651				6.5182	
BO+AD+NONAD	0.2570				6.5182	
BO+AD+NONAD+CG	0.2684				$6.5182 - 11.9147\alpha^2$	
BO+AD+NONAD+BP	0.2737		$0.4627\alpha^2$		$6.5182 - 7.9152\alpha^2$	
BO+AD+BP+QED(3)-AS	0.2741		$0.4627\alpha^2$		$6.5182 - 7.9152\alpha^2 + 106.3128\alpha^3$	
BO+AD+BP+QED(3)	∞	$-\frac{7}{6}\pi\alpha^3$	$0.4627\alpha^2$	$-7\pi\alpha^3$	$6.5182 - 7.9152\alpha^2 + 106.3128\alpha^3$	
BO+AD+BP+QED(3)+CP	0.2732			$-7\pi\alpha^3$	$-3.9995\alpha^2$	$\neq 0$

Pseudopotentials as a compromise solution for intermediate Z values

★ Good points

- Pseudopotentials are fitted to the experimental data, so probably all scalar relativistic effects are potentially included
- Relativistic terms involving the electronic and nuclear spins can be introduced a posteriori
- Nonrelativistic QED theory should work
- Retardation effects correct in the limit of “small” and large interatomic distances
- Optimized basis sets are available
- No new integrals are necessary

★ Bad points

- Optimized for atomic excitation energies, do not need to perform well for molecules
- Introduce semi-empirical elements into the theory

Challenges for theoreticians and experimentalists

- ★ molecular gerade/ungerade mixing

$$\hat{H}_{\text{FCI}} = K \sum_{i=1}^N \vec{s}_i \cdot \left[\vec{l}_1 \delta(\mathbf{r}_i - \mathbf{R}_A) + \vec{l}_2 \delta(\mathbf{r}_i - \mathbf{R}_B) \right]$$

- ★ finite size nuclear corrections

$$\hat{H}_{\text{fsn}} = \frac{2\pi}{3} \sum_{i=1}^N \sum_a Z_a \delta(\mathbf{r}_i - \mathbf{R}_a) \langle \rho^2 \rangle$$

- ★ QED at the α^4 level

No mathematically sound expression available. Equations for atoms cannot be generalized to molecules by lowering the symmetry (as it was done in the α^3 case), because divergent integrals appear that cannot be regularized.

- ★ long-range strong interactions

$$V_{\text{nucl}}(R) \sim \frac{C_6^{\text{nucl}}}{R^6}$$

Challenges for theoreticians and experimentalists

- ★ Retardation effects at large distances
 - interaction of two ground state S atoms

$$E_{\text{disp}}^{(2)}(\text{ret}) = -\frac{1}{\pi R^6} \int_0^\infty \alpha_0^2(i\omega) \exp(-2\omega\alpha R) P(\omega\alpha R) d\omega,$$

- first-order resonant interaction of S+P identical atoms

$$E_{\text{res}}^{(1)}(\text{ret}) = -\frac{C_3^{\text{res}}}{R^3} \left[3 \cos(\omega\alpha R) + 3\omega\alpha R \sin(\omega\alpha R) - (\omega\alpha R)^2 \sin^2(\omega\alpha R) \right]$$

- second-order resonant interaction of $S_{\text{gs}} + S_{\text{exc}}$ identical atoms

$$E_{\text{res}}^{(2)}(\text{ret}) \sim -\frac{C_2^{\text{res}}}{R^2} \left[\frac{\omega^4 \alpha^3}{12R} \cos(\omega\alpha R) + \frac{\omega^5 \alpha^4}{60} \sin(\omega\alpha R) \right] + \dots$$

Preliminary results for the $a^3\Sigma_u^+$ state of Li_2

- ★ state-of-the-art fit to the experimental data (Bob LeRoy 2011)

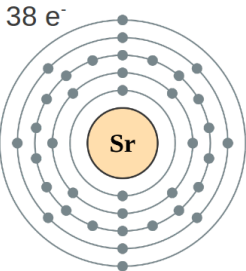
${}^7,7\text{Li}_2$	$R_e = 4.17005(3) \text{ \AA}$	$D_e = 333.758(7) \text{ cm}^{-1}$
${}^6,6\text{Li}_2$	$\Delta R_e = -0.000012(3) \text{ \AA}$	$\Delta D_e = 0.020(4) \text{ cm}^{-1}$
- ★ preliminary *ab initio* results

method/basis	aDZ+mid	aTZ+mid	aQZ+mid	a5Z+mid	extrap.	empirical
CCSDT	-343.574	-340.130	-341.237	-338.106	-334.880	-333.758
CCSDTQ	1.574				-333.306	-333.758
CCSDTQP6	???					
mass-dependent	-0.0908	-0.0870	-0.0961	-0.1015	-333.408	-333.758
ΔD_e	0.015	0.014	0.016	0.017	—	0.020(4)
relativistic	???					
QED	???					

Preliminary results for the $a^3\Sigma_u^+$ state of Li_2

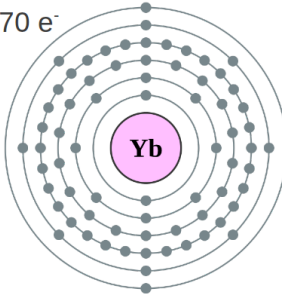
- ★ theoretical prospects
 - CCSDTQ large basis, YES
 - CCSDTQP6, YES, but small basis
 - relativistic α^2 , YES, but at the CCSDT level
 - QED α^3 , YES, but with the atomic Bethe logarithm (good approximation for H_2), and the Araki-Sucher term neglected
- ★ possible theoretical predictions
 - molecular gerade/ungerade mixing
 - long-range retardation

Strontium and Ytterbium

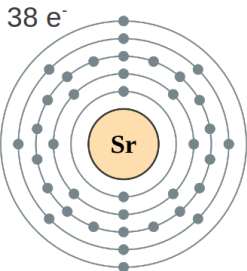


1	IA																0									
1	H																	He								
2	Li Be																		B C N O F Ne							
3	Na Mg		IIA		IIIB	IVB	VB	VIB	VIB	VII					IB	IB						Ar				
4	K Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr								
5	Rb Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe								
6	Cs Ba		*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn								
7	Fr Ra		+Ac	Rf	Ha	Hs	Mt	110	111	112	113															

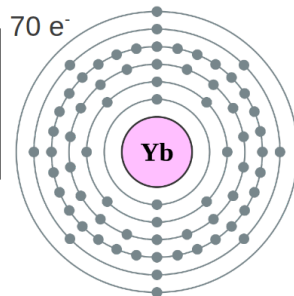
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+	90	91	92	93	94	95	96	97	98	99	100	101	102
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Lr



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4	K Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																																																									
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Sr₂ and SrYb molecules from two **closed-shell** atoms:

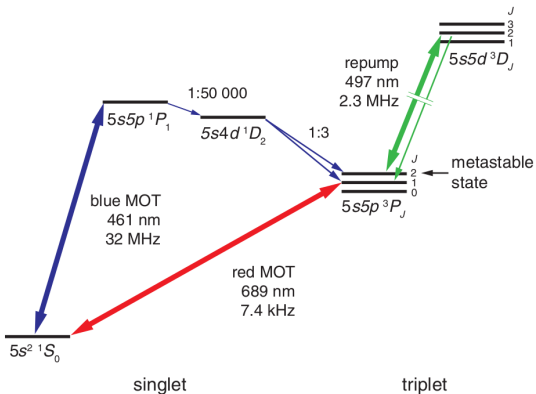
- ★ magnetoassociation, laser cooling and sympathetic cooling are not feasible
- ★ simple molecular potentials (no hyperfine structure)
- ★ double-stage Doppler cooling needed

What has been achieved so far?

- ★ BEC of ^{174}Yb - *PRL*, **91**, 040404 (2003)
- ★ BEC of ^{84}Sr - *PRL*, **103**, 200401 and 200402 (2009)

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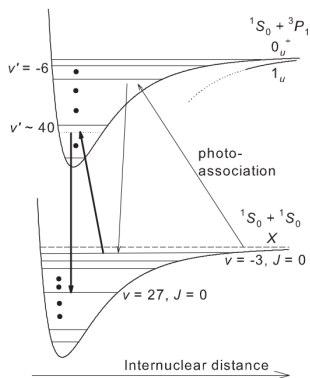
Efficient double-stage Doppler cooling

What has been achieved so far?

- ★ PA near the $^1S_0 - ^3P_1$ intercombination transition for Yb_2 - *PRL*, **96**, 153201 (2006) and Sr_2 - *PRL*, **96**, 203201 (2006)

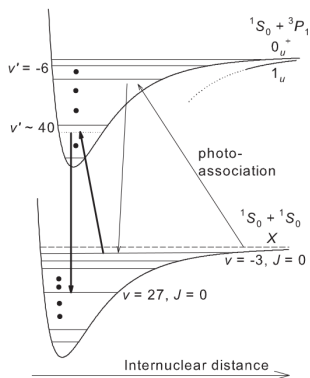
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Why ultracold Sr₂ molecules?

- ★ precision measurements & test of fundamental symmetries

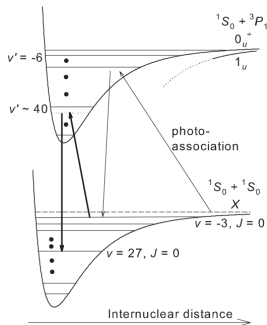
time dependence of $\mu = m_e/m_p$

$$\frac{\Delta\mu}{\mu} = \frac{\Delta\nu}{\nu}$$

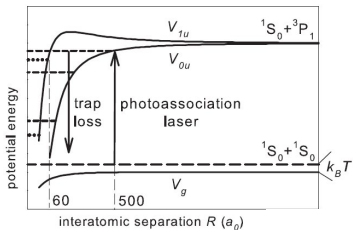
ν transition frequencies

cold \triangleq long observation times

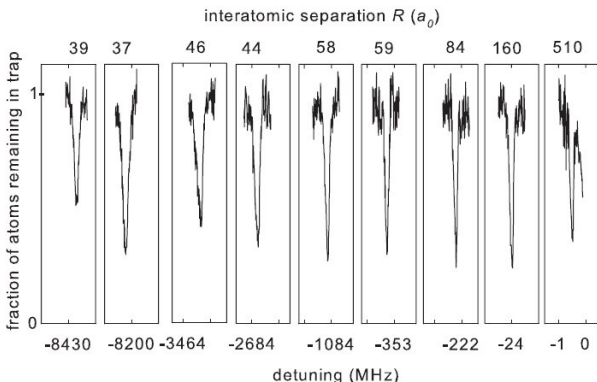
Zelevinsky, Kotochigova, Ye,
PRL 100, 043201 (2008)



Photoassociation of Sr₂



Zelevinsky et al., Phys Rev Lett 96, 203201 (2006)



Quantum chemical methods

Methods:

- ★ Coupled Cluster + BSSE
 - interaction energy curves
 - permanent and transition dipole moments
- ★ Multireference Configuration Interaction
 - spin-orbit coupling
 - (partly) long-range coefficients

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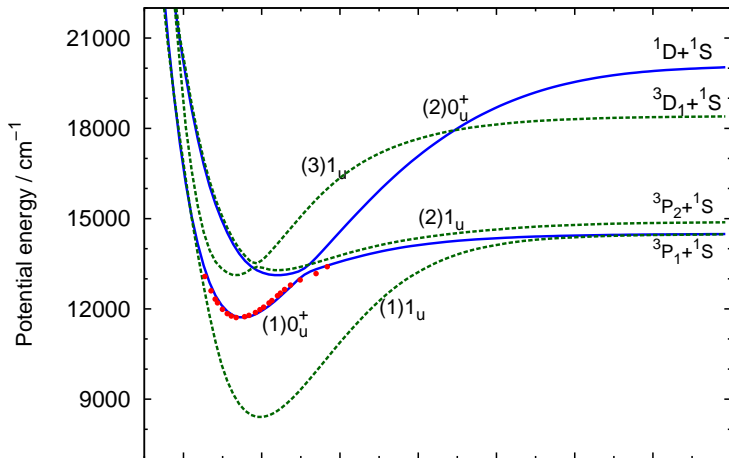
Energy-Consistent Pseudopotentials and basis:

- ★ Sr - ECP28MDF + [14s13p6d5f2g|8s10p6d5f2g]
- ★ + a large set of *spdfg* bond functions

Photoassociation of Sr₂

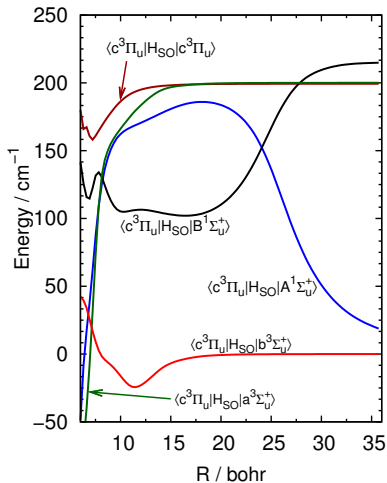
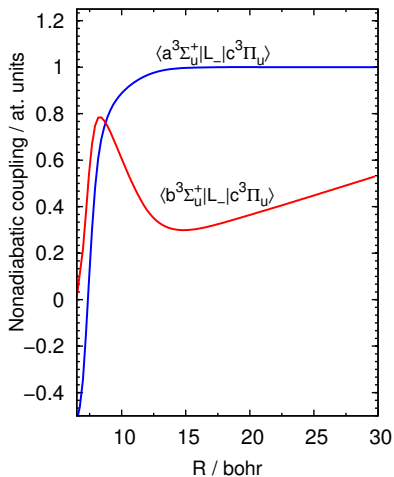
Skomorowski, Pawlowski, Koch, Moszynski, *J Chem Phys* 136, 194396 (2012)

experimental data: Stein, Knöckel, Tiemann, *Eur Phys J D*, 64, 227 (2011)



Photoassociation of Sr₂

Skomorowski, Pawlowski, Koch, Moszynski, *J Chem Phys* 136, 194396 (2012)



Accuracy of the *ab initio* predictions

- ★ Comparison of the spectroscopic characteristics of the available potentials

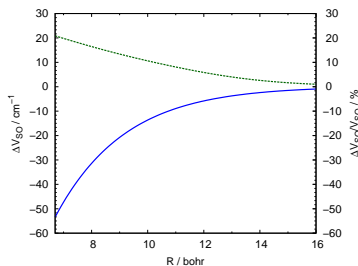
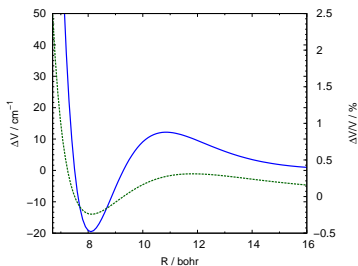
State	D_e/cm^{-1}	R_e/bohr	Ref.	Dissociation
(1)0 _u ⁺	2782	7.51	Present	³ P ₁ + ¹ S
	2790	7.46	Tiemann 2011	
	1837	8.2	other theory	
(2)0 _u ⁺	7039	8.39	Present	¹ D ₂ + ¹ S
	5292	7.2	other theory	
(1)1 _u	6097	7.95	Present	³ P ₁ + ¹ S
	6921	7.8	other theory	
(2)1 _u	1942	7.34	Present	³ P ₂ + ¹ S
	1907	8.2	other theory	
(3)1 _u	4863	7.97	Present	³ D ₁ + ¹ S
	4849	7.4	other theory	

Accuracy of the *ab initio* predictions

- ★ RMSD of all rovibrational levels with respect to the experimental data of Tiemann and coll. for J' up to and including 219: 10.5 cm^{-1}
- ★ RMSD of all rovibrational levels with respect to the experimental data of Tiemann and coll. after adjusting in the analytical fit the repulsive wall parameter A_0 by 0.03% and the C_{12} attractive coefficient: 0.64 cm^{-1}
- ★ Least bound levels measured by Zelevinsky et al. reproduced within the experimental error bars

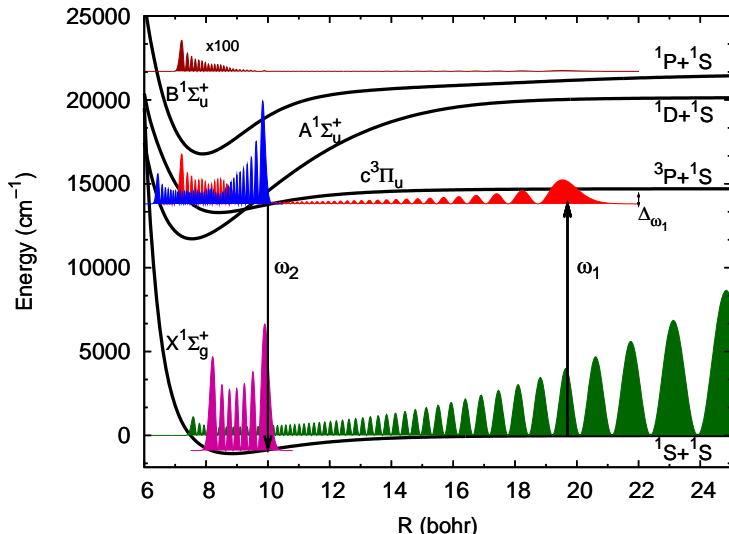
Accuracy of the *ab initio* predictions

Left panel: Comparison of the original $A^1\Sigma_u^+$ potential with the fitted in the present work to the experimental data for $J' = 1$. The solid blue line shows the absolute difference, $\Delta V = V_{\text{fitted}} - V_{ab \text{ initio}}$, while the the green dashed line shows the relative difference, $\frac{\Delta V}{V} = \frac{V_{ab \text{ initio}} - V_{\text{fitted}}}{V_{ab \text{ initio}}} \cdot 100\%$. Right panel: the same for the spin-orbit coupling parameter $\xi_2 = \langle c^3\Pi_u | H_{SO} | B^1\Sigma_u^+ \rangle$.



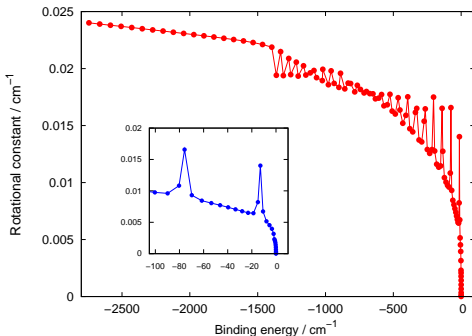
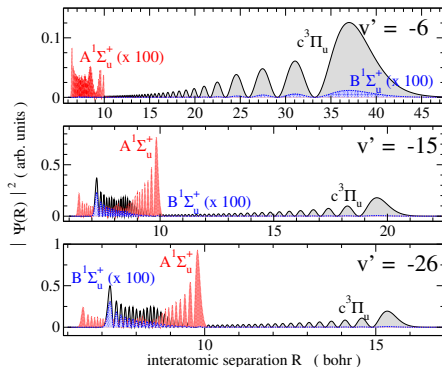
Proposed photoassociation scheme for Sr₂

Skomorowski, Moszynski, Koch, Phys Rev A 85, 043414 (2012)

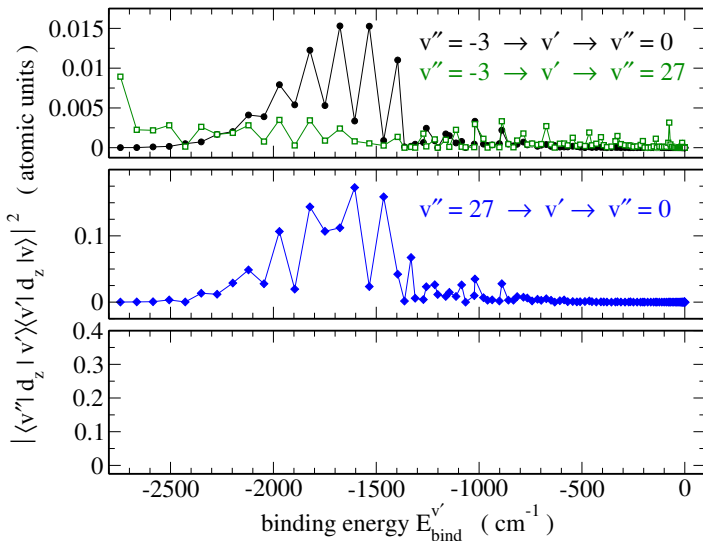


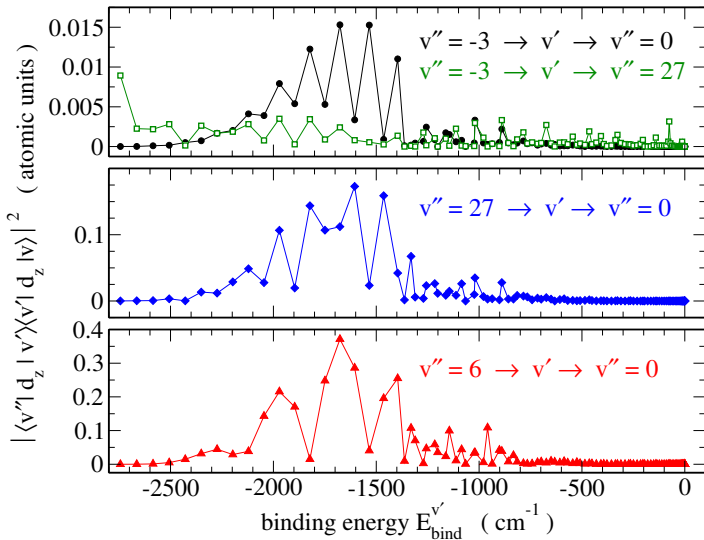
Efficient transitions to $X^1\Sigma_g^+(v=0)$ through the resonant spin-orbit coupling

Skomorowski, Pawłowski, Koch, Moszynski, *J Chem Phys* 139, 194396 (2012)
 Skomorowski, Moszynski, Koch, *Phys Rev A* 85, 043414 (2012)



- ★ resonantly perturbed levels facilitate Raman transitions
- ★ they exist in large part of excited state vibrational spectrum

Raman transitions to $X^1\Sigma_g^+(v=0)$ 

Efficient Raman transitions to $v = 0$ 

Conclusions

- ★ Precision calculations are nowadays feasible for few-body systems, and with some restrictions to light many-body systems.
- ★ For heavier systems some approximations like the use of pseudopotentials is necessary, but with a proper choice of methods and basis sets, semi-quantitative agreement with the experiment can be reached, and the remaining discrepancies removed by fine tuning of the *ab initio* results. Still, the *ab initio* results are very useful to guide the ongoing experiments.
- ★ All these problems will soon be overcome with the new software from Warsaw:
KOŁOS: a general purpose *ab initio* program for the electronic structure calculations with Slater orbitals, and explicitly correlated Slater geminals and Kołos-Wolniewicz functions.