Nuclear size effects in rotational spectra: a tale with a twist

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with thanks to ....

Stefan Knecht (Odense)

Rovibrational spectroscopy of diatomic molecules

- Within the Born-Oppenheimer ("clamped nuclei") approximation: **rotating vibrator**

$$\left[-\frac{\hbar^2}{2\mu}\frac{d}{dR^2} + E^{el}(R) + \frac{\hbar^2 J(J+1)}{2\mu R^2} \right] \psi_{\nu,J}(R) = E_{\nu,J}\psi_{\nu,J}(R) \qquad (1)$$

- Solutions were provided by Dunham in 1932 in the framework of the Jeffreys–Wentzel–Kramers–Brillouin (JWKB) approximation[1]

$$E_{\nu J} = h \sum_{kl} Y_{kl} \left(\nu + \frac{1}{2} \right)^k J^l (J+1)^l$$
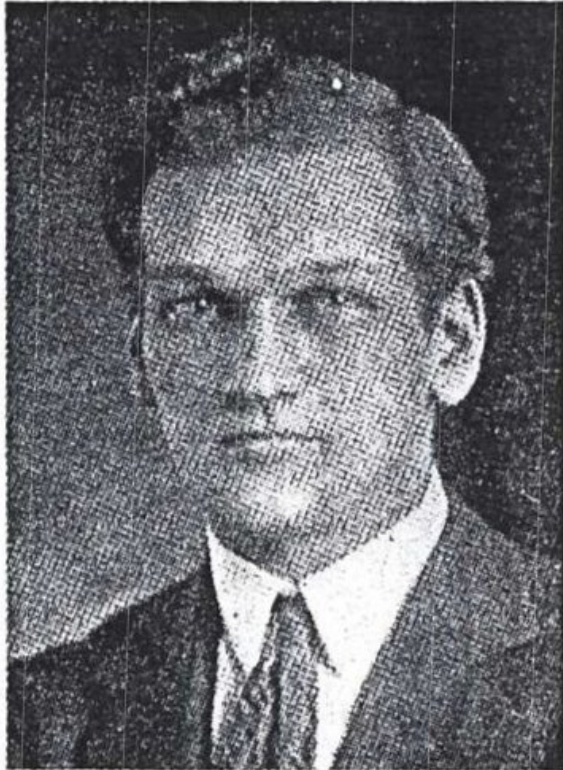
where ν is the vibrational and J the rotational quantum number.

$$
\begin{array}{rcll}
Y_{10} & = & \frac{\omega_e}{2\pi} \left[1 + \left(B_e^2/4\omega_e^2 \right) [\ldots] \right] & \approx \quad \nu_e \qquad \text{(harmonic oscillator)} \\[2mm]
Y_{01} & = & B_e \left[1 + \left(B_e^2/2\omega_e^2 \right) [\ldots] \right] & \approx \quad B_e \qquad \text{(rigid rotator)}
\end{array}
$$

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[1]J. L. Dunham, Phys. Rev. **41**(1932) 721

Digression: James Lawrence Dunham

The Energy Levels of a Rotating Vibrator

By J. L. DUNHAM

Harvard University

The energy levels of a rotating vibrator are calculated in considerable detail by means of the Wentzel-Brillouin-Kramers method. The new terms determined are $\omega_e z$ and a set of correction terms which appear in the earlier members of the equation. These correction terms enter in such a way that ω_e is not exactly the coefficient of $(v+\frac{1}{2})$; B_e is not exactly the coefficient of $K(K+1)$, etc. However the differences are small and are detectable only in the case of light molecules. The correction terms are of the magnitude of B_e^2/ω_e^2. Formulas for the effect of the correction terms on isotope shifts are given, and for the calculation of the correction terms themselves. Also a method is given for obtaining actual potential functions from band spectrum data, based on Morse's potential function. Finally the numerical magnitude of the correction terms for several states of H_2 and for NaH is discussed.

1904 Born March 27 in New York; attended Scarsdale High School

1929 PhD at Harvard University:
Intensity of lines in the harmonic band of hydrogen chloride in the near infra-red

1933 instructor in physics at Harvard;
dies May 3 in Cambridge (Mass.) from pulmonary infarct following appendectomy

Isotopic mass shift

- Dunham (1932)

$$
\left.\begin{array}{rcl}
\omega_e &=& \sqrt{\dfrac{k_e}{\mu}} \\[2ex]
B_e &=& \dfrac{\hbar}{2\mu R_e^2}
\end{array}\right\} \quad \Rightarrow \quad Y_{kl} = \mu^{-(k/2+l)} U_{kl}
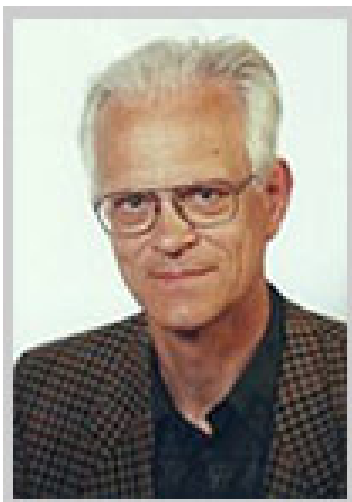$$

- Watson(1980)[2]

$$
Y_{kl} = \mu^{-(k/2+l)} U_{kl} \left[1 + m_e \left(\frac{\Delta_{kl}^A}{M_A} + \frac{\Delta_{kl}^B}{M_B} \right) \right]
$$

Δ_{kl}^X - mass-independent atom-specific correction factors

- Δ_{kl}^a: adiabatic contribution: mass-dependent potential $E^{el}(R)$

- Δ_{kl}^{na}: non-adiabatic contribution: coupling of electronic states

[2]A. H. M. Ross, R. S. Eng, H. Kildal, Opt. Comm. **12** (1971) 433; J. K. G. Watson, J. Mol. Spect. **80** (1980) 411

Anomalies

OBSERVED ADIABATIC CORRECTIONS TO THE BORN–OPPENHEIMER APPROXIMATION FOR DIATOMIC MOLECULES WITH TEN VALENCE ELECTRONS

E. TIEMANN

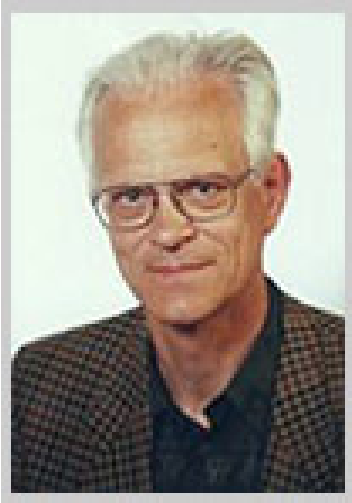Institut A für Experimentalphysik, Universität Hannover, D-3000 Hannover, FRG

and

H. ARNST, W.U. STIEDA, T. TÖRRING and J. HOEFT

Institut für Molekülphysik, Freie Universität Berlin, D-1000 Berlin 33, FRG

Molecule/atom	Δ_{01}	Δ_{01}^{Dunham}	Δ_{01}^{nonad}	Δ_{01}^{ad}	r_e^{BO} (Å)
parameters belonging to atoms of the group III and VI					
CO/C	−2.061(34) [a]	−0.01526(6) [b]	−1.8484(36) [b]	−0.197(35)	1.1282291(14)
CS/C	−2.596(49) [c]	−0.0148	−2.4758 [d]	−0.105(55)	1.5348224(23)
SiS/Si	−1.392(59) [e]	−0.0106	−1.1760 [f]	−0.205(69)	1.9292639(19)
GeS/Ge	−1.463(70) [g]	+0.0008	−1.2244 [f]	−0.239(70)	2.0120431(10)
GeSe/Ge	−1.612(46) [g]	−0.0086	−1.2812 [f]	−0.322(46)	2.1346018(10)
SnS/Sn	−1.76(19)	+0.0058	−1.0608 [f]	−0.70(19)	2.2089829(22)
SnSe/Sn	−1.555(84)	−0.0076	−1.1290 [f]	−0.419(84)	2.3255738(11)
SnTe/Sn	−1.749(97)	−0.0114	−1.1962 [f]	−0.541(97)	2.5227979(13)
PbS/Pb	−12.94(141) [h]	+0.0090	−1.2056 [f]	−11.74(141)	2.2867844(40)
PbSe/Pb	−11.86(92)	−0.0236	−1.1726 [f]	−10.66(92)	2.4021776(24)
PbTe/Pb	−11.98(81)	−0.0366	−1.1596 [f]	−10.78(81)	2.5949253(27)
GaF/Ga	−0.60(30)	−0.093	−0.4384 [d]	−0.07(30)	1.7743351(25)
GaI/Ga	−0.706(96) [i]	−0.0182	−0.50(30) [k]	−0.19(30)	2.5746263(40)
InI/In	−2.68(27)	−0.0066	−0.30(30) [k]	−2.37(45)	2.753618(10)
TlF/Tl	−18.76(110)	+0.0100	−0.1516 [d]	−18.61(110)	2.084386(10)
TlCl/Tl	−18.96(200)	−0.0040	−0.1860 [d]	−18.76(200)	2.484739(10)
TlBr/Tl	−15.61(46)	−0.0216	−0.05(30) [k]	−15.55(75)	2.6181114(15)
TlI/Tl	−14.68(47)	−0.0172	−0.05(30) [k]	−14.61(75)	2.813614(10)

Unusually large adiabatic mass corrections observed for lead/thallium compounds

Isotopic field shift

ISOTOPIC FIELD SHIFT OF THE ROTATIONAL ENERGY
OF THE Pb-CHALCOGENIDES AND Tl-HALIDES

J. SCHLEMBACH and E. TIEMANN
Institut A für Experimentalphysik, Universität Hannover, D-3000 Hannover, FRG

$$Y_{kl} = \mu^{-(k/2+l)} U_{kl} \left[1 + m_e \left(\frac{\Delta_{kl}^A}{M_A} + \frac{\Delta_{kl}^B}{M_B} \right) + V_{kl}^A \delta \left\langle r^2 \right\rangle_{AA'} + V_{kl}^B \delta \left\langle r^2 \right\rangle_{BB'} \right]$$

$\delta \left\langle r^2 \right\rangle_{XX'}$ change in mean squared nuclear charge radius between isotope X '
and reference isotope X

V_{kl}^X correction factor due to the finite size of nucleus X

Isotopic field shift on rotational constant

Focus on the rotational constant

$$Y_{01} = \mu^{-1} U_{01} \left[1 + m_e \left(\frac{\Delta_{01}^A}{M_A} + \frac{\Delta_{01}^B}{M_B} \right) + V_{01}^A \delta \left\langle r^2 \right\rangle_{AA'} + V_{01}^B \delta \left\langle r^2 \right\rangle_{BB'} \right]$$

for which the correction factor reads

$$V_{01}^X = \frac{Z_X e^2}{3\epsilon_0 k_e R_e} \left(\frac{d\rho_0^X}{dR} \right)_{R_e} ; \quad X = A, B$$

Table 2

Differential coefficient of the electron density from the function of the internuclear distance at the nucleus Pb or Tl, calculated with the values of table 1

Molecule AB	$(d\rho/dR)_{R_e}^A$ (A^{-4})	Molecule AB	$(d\rho/dR)_{R_e}^A$ (A^{-4})
PbS	213(17)	TlF	254(30)
PbSe	177(15)	TlCl	185(25)
PbTe	148(11)	TlBr	142.0(42)
		TlI	120.6(38)

A computational study

S. A. Cooke, M. C. L. Gerry and D. P. Chong, Chem. Phys. **298** (2004) 205:

Density functional theory (DFT) calculations using the long-range corrected functional SAOP and the Zeroth Order Regular Approximation (ZORA) Hamiltonian

Derivative of the electron density at the metal nucleus with respect to the internuclear separation calculated using the SAOP method at the equilibrium bond length in units of Å^{-4}

Molecule	SAOP				Experiment [12,13][a]
	DZ	TZP	TZ2P	QZ4P	
PbO				40.3	_[b]
PbS	40.8	31.7	67.3	27.8	23.19(46)
PbSe	38.8	20.1	25.5	25.6	17.7(15)
PbTe	39.5	23.7	31.5	21.1	14.8(11)
TlF	71.8	97.1	107.3	44.4	25.4(30)
TlCl	35.6	45.8	73.8	36.7	18.5(25)
TlBr	28.8	32.4	46.8	26.5	14.20(42)
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TlI	23.9	25.0	34.7	21.1	12.06(38)

[a] Experimental values taken from [12] have been corrected in light of an error pointed out in [13].

A mysterious correction factor
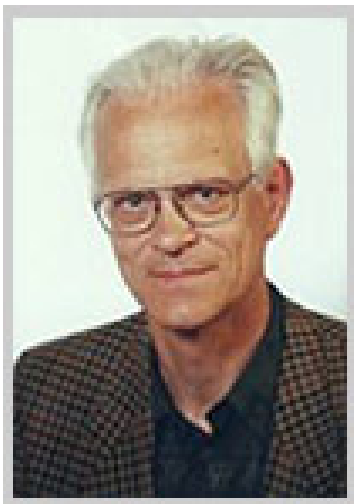
MOLECULAR-BEAM–LASER STUDIES OF THE STATES X $^1\Sigma^+$ AND A0$^+$ OF PbS

H. KNÖCKEL, T. KRÖCKERTSKOTHEN and E. TIEMANN

Institut für Atom- und Molekulphysik, Universität Hannover, D-3000 Hannover, FRG

☆ There is a computational error in table 2 of ref. [2]: the value of ρ'_{el} should be reduced by a factor of 10.

We note that the expression for the finite nuclear size correction factor is modified:

$$V_{01}^X \quad \rightarrow \quad \pi^2 V_{01}^X$$

4-component relativistic Hamiltonians

- Generic form of electronic Hamiltonian:

$$H = \sum_i h(i) + \frac{1}{2} \sum_{i \neq j} g(i,j) + V_{NN}; \quad h(i) = h_0 + V_{eN}$$

- One-electron operator: Dirac operator in the molecular field

$$\hat{h}_D(i) = \beta'_i mc^2 + c(\boldsymbol{\alpha}_i \cdot \mathbf{p}_i) + \hat{V}_{eN}; \qquad \beta' = \beta - 1$$

- Two-electron operator: (Coulomb gauge)

$$\hat{g}(i,j) = \frac{1}{r_{ij}}$$

$$- \frac{c\boldsymbol{\alpha}_i \cdot c\boldsymbol{\alpha}_j}{c^2 r_{ij}} - \frac{(c\boldsymbol{\alpha}_i \cdot \boldsymbol{\nabla}_i)(c\boldsymbol{\alpha}_j \cdot \boldsymbol{\nabla}_j) r_{ij}}{2c^2}$$

$$+ \cdots$$
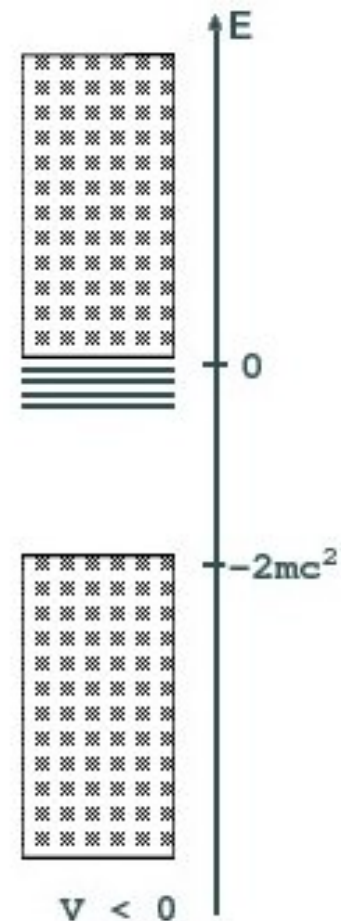
From 4 to 2 components

- Unitary transformation: decoupling and renormalization

$$\widehat{U}^{\dagger} \begin{bmatrix} V & c\,(\boldsymbol{\sigma} \cdot \mathbf{p}) \\ c\,(\boldsymbol{\sigma} \cdot \mathbf{p}) & V - 2mc^2 \end{bmatrix} \widehat{U} = \begin{bmatrix} \hat{h}+ & 0 \\ 0 & \hat{h}_- \end{bmatrix}; \quad \widehat{U} = \begin{bmatrix} \Omega_+ & -\chi^{\dagger}\Omega_- \\ \chi\Omega_+ & \Omega_- \end{bmatrix}$$

- Transformation of orbitals:

$$\begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} \quad \rightarrow \quad \begin{bmatrix} \Omega_+ \left[\psi^L + \chi^{\dagger}\psi^S\right] \\ \Omega_- \left[\psi^S - \chi\psi^L\right] \end{bmatrix}$$

- Positive-energy solutions: χ is the exact coupling of the large and small components

$$\psi^S = \chi\psi^L; \quad \chi = \left(2mc^2 - V + E\right)^{-1} c\,(\boldsymbol{\sigma} \cdot \mathbf{p})$$

- Approximate Hamiltonians, e.g. ZORA

$$\chi = \frac{c}{2mc^2 - V} \left[1 + \frac{E^+}{2mc^2 - V}\right]^{-1} (\boldsymbol{\sigma} \cdot \mathbf{p}) \sim \frac{c}{2mc^2 - V} (\boldsymbol{\sigma} \cdot \mathbf{p})$$

Decoupling the easy way

M. Iliaš and T. Saue , J. Chem. Phys. **126** (2007) 064102;

W. Kutzelnigg and W. Liu, *J. Chem. Phys.* **123** (2005) 241102;

M. Iliaš, H. J. Aa. Jensen, V. Kellö, B. O. Roos and M. Urban, *Chem. Phys. Lett.* **408** (2005) 210

1. Solve the Dirac equation on matrix form

2. Extract the coupling χ from the solutions

3. Construct the transformation matrix U, next h^{X2C}

Advantages:

- reproduces exactly the positive-energy spectrum of the Dirac Hamiltonian

- all matrix manipulations; no new operators to program

- explicit representation of transformation matrix;
  any property operator can be transformed on the fly, no picture change errors

Note: SO-corrections to the 2-electron interaction are handled by the AMFI approach
(B. A. Heß, C. M. Marian, U. Wahlgren and O. Gropen, Chem. Phys. Lett **251** (1996) 365)

Picture change errors

The 2-component Hamiltonian is obtained as

$$H^{2c} = \left[U^\dagger H^{4c} U\right]_{++}$$

Property operators Ω^{4c} must be subjected to the same decoupling transformation as the Hamiltonian, that is

$$\Omega^{2c} = \left[U^\dagger \Omega^{4c} U\right]_{++}$$

Use of the approximate expression

$$\Omega^{2c} \approx \left[\Omega^{4c}\right]_{LL}$$

leads to picture change errors that may be larger than the relativistic effects !

E.
J. Baerends, W. H. E. Schwarz, P. Schwerdtfeger and J. G. Snijders, J. Phys. B. **23**(1990) 3225; V. Kellö and A. J. Sadlej, Int. J. Quant. Chem. **68** (1998) 159; M. Pernpointer and P. Schwerdtfeger, Chem. Phys. Lett. **295**(1998) 347; V. Kellö and A. J. Sadlej, Theoret. Chim. Acta **547**(2001) 35; J. Seino, W. Uesugi and M. Hada, J. Chem. Phys. **132** (2010) 164108

An example: the electron density

$$\rho^{4c}\left(\boldsymbol{P}\right) \;=\; -e\sum_i \left\langle \psi_i^{4c} \left| \delta\left(\boldsymbol{r}-\boldsymbol{P}\right)\right| \psi_i^{4c}\right\rangle \qquad\qquad =\; -e\sum_i \psi_i^{4c\dagger}\left(\boldsymbol{P}\right)\psi_i^{4c}\left(\boldsymbol{P}\right)$$

$$\rho^{2c}\left(\boldsymbol{P}\right) \;=\; -e\sum_i \left\langle \psi_i^{2c} \left| \left[U^\dagger\delta\left(\boldsymbol{r}-\boldsymbol{P}\right)U\right]_{++}\right| \psi_i^{2c}\right\rangle \;\neq\; -e\sum_i \psi_i^{2c\dagger}\left(\boldsymbol{P}\right)\psi_i^{2c}\left(\boldsymbol{P}\right)$$

$\sum_i \psi_i^{4c\dagger}\psi_i^{4c}$ *vs.* $\sum_i \psi_i^{2c\dagger}\psi_i^{2c}$ *for the mercury atom*

An example: the electron density

$$\rho^{4c}\left(\boldsymbol{P}\right) = -e\sum_i \left\langle \psi_i^{4c} \left| \delta\left(\boldsymbol{r}-\boldsymbol{P}\right)\right| \psi_i^{4c} \right\rangle \qquad = -e\sum_i \psi_i^{4c\dagger}\left(\boldsymbol{P}\right)\psi_i^{4c}\left(\boldsymbol{P}\right)$$

$$\rho^{2c}\left(\boldsymbol{P}\right) = -e\sum_i \left\langle \psi_i^{2c} \left| \left[U^\dagger \delta\left(\boldsymbol{r}-\boldsymbol{P}\right)U\right]_{++}\right| \psi_i^{2c} \right\rangle \neq -e\sum_i \psi_i^{2c\dagger}\left(\boldsymbol{P}\right)\psi_i^{2c}\left(\boldsymbol{P}\right)$$
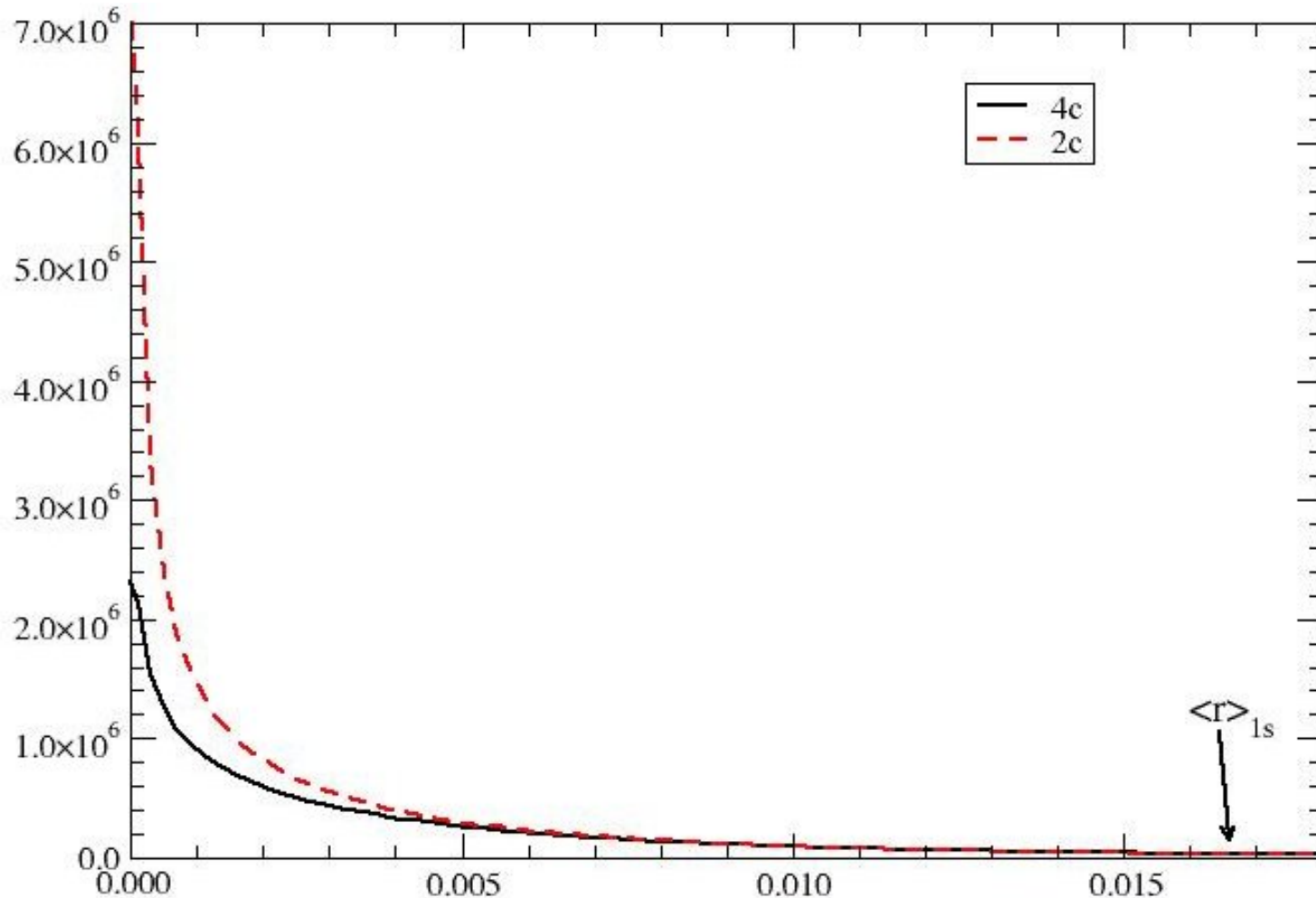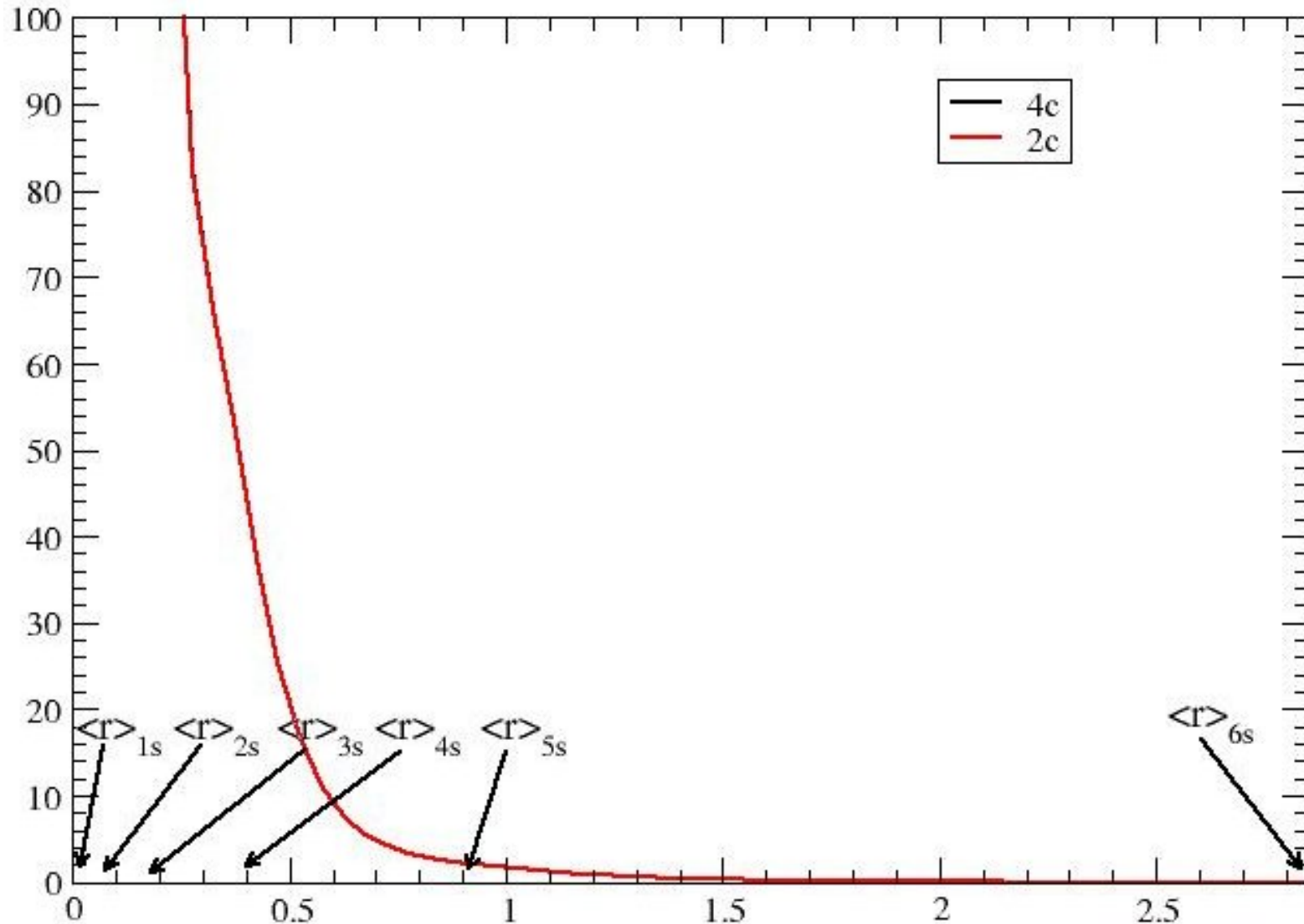

$\sum_i \psi_i^{4c\dagger}\psi_i^{4c}$ vs. $\sum_i \psi_i^{2c\dagger}\psi_i^{2c}$ for the mercury atom

An example: the electron density

$$\rho^{4c}(\boldsymbol{P}) \quad = \quad -e\sum_i \langle \psi_i^{4c} | \delta(\boldsymbol{r} - \boldsymbol{P}) | \psi_i^{4c} \rangle \qquad\qquad = \quad -e\sum_i \psi_i^{4c\dagger}(\boldsymbol{P})\,\psi_i^{4c}(\boldsymbol{P})$$

$$\rho^{2c}(\boldsymbol{P}) \quad = \quad -e\sum_i \left\langle \psi_i^{2c} \left| \left[U^\dagger \delta(\boldsymbol{r} - \boldsymbol{P})\,U\right]_{++} \right| \psi_i^{2c} \right\rangle \quad \neq \quad -e\sum_i \psi_i^{2c\dagger}(\boldsymbol{P})\,\psi_i^{2c}(\boldsymbol{P})$$

$\sum_i \psi_i^{4c\dagger}\psi_i^{4c}$ vs. $\sum_i \psi_i^{2c\dagger}\psi_i^{2c}$ for the mercury atom

Thallium iodine ($R_e = 2.8136$ Å): relativistic effects

Method	Basis	Hamiltonian	Approach	ρ_0^{Tl}(Å^{-3})	$d\rho_0^{Tl}/dR\big|_{R=R_e}$(Å^{-4})
SAOP	TZ	4c	$\langle\rho^{Tl}\rangle$	17153354.69	118.14
SAOP	TZ	NR	$\langle\rho^{Tl}\rangle$	2535515.16	24.50
				-85.2%	-79.3%

Tl

I

Thallium iodine ($R_e = 2.8136$ Å): picture change errors

Method	Basis	Hamiltonian	Approach	$\rho_0^{Tl}(\text{Å}^{-3})$	$d\rho_0^{Tl}/dR\big|_{R=R_e}(\text{Å}^{-4})$
SAOP	TZ	4c	$\langle\rho^{Tl}\rangle$	17153354.69	118.14
SAOP	TZ	X2C	$\psi^\dagger\psi$	54950057.82	788.15
				+220.3%	+567.1%

The picture change error is larger than the relativistic effect !
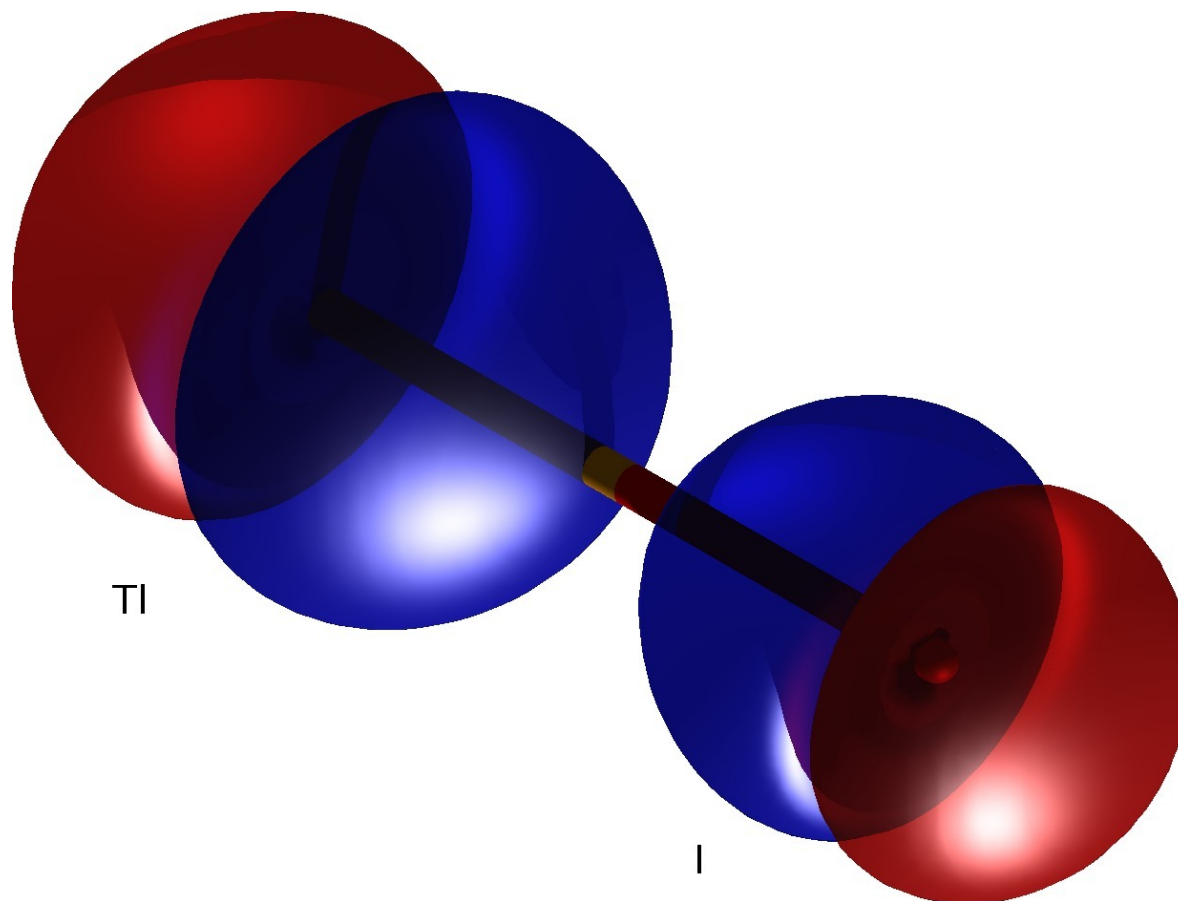
Thallium iodine ($R_e = 2.8136$ Å): picture change errors

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SAOP	TZ	X2C	$\langle\rho^{Tl}\rangle$	17153358.65	118.24

The picture change error is eliminated by correct transformation of the property operator.
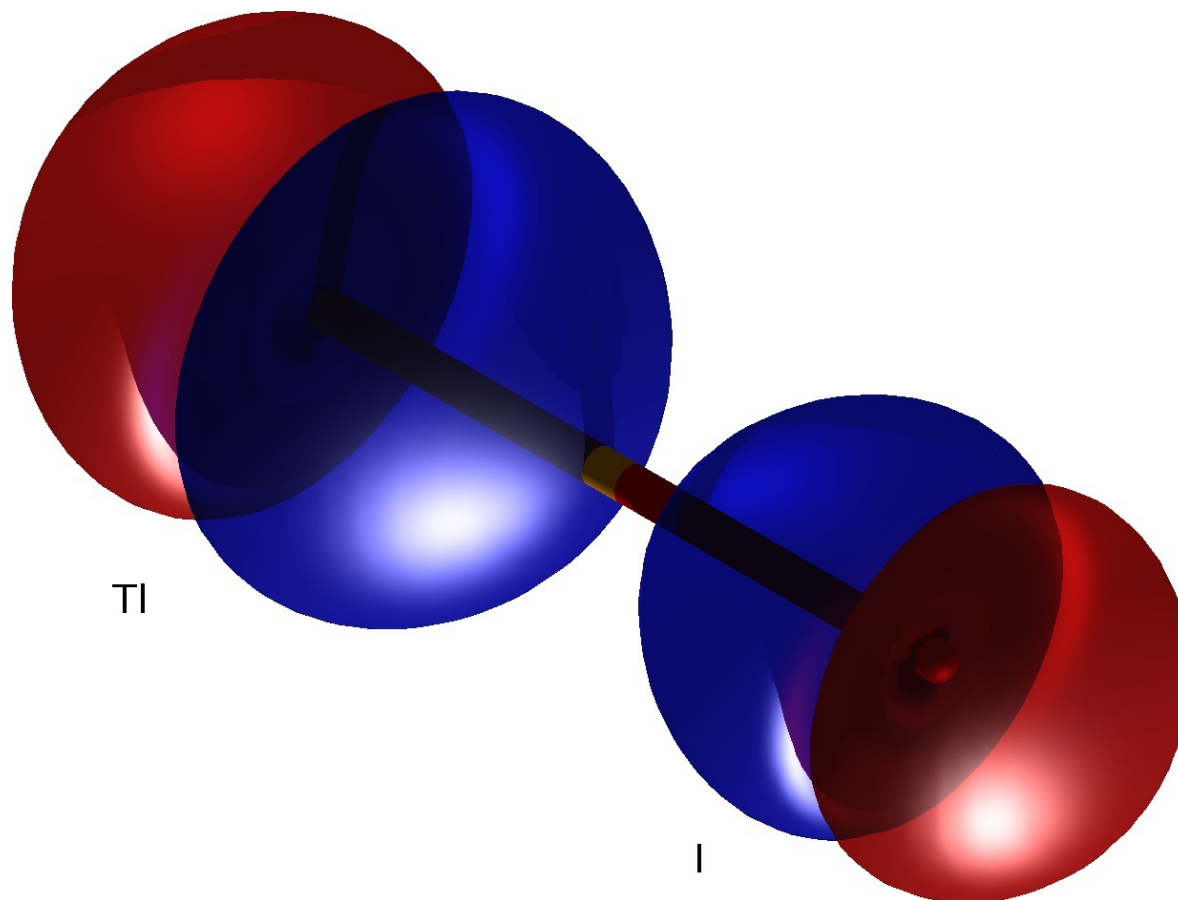
Thallium iodine ($R_e = 2.8136$ Å): comparing with experiment

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SAOP	TZ	4c	$\langle \rho^{Tl} \rangle$	17153354.69	118.14
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Table 2

Differential coefficient of the electron density from the function of the internuclear distance at the nucleus Pb or Tl, calculated with the values of table 1

Molecule AB	$(d\rho/dR)^A_{R_e} (\text{A}^{-4})$	Molecule AB	$(d\rho/dR)^A_{R_e} (\text{A}^{-4})$
PbS	213(17)	TlF	254(30)
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Thallium iodine ($R_e = 2.8136$ Å): comparing with calculations

Method	Basis	Hamiltonian	Approach	$\rho_0^{Tl}(\text{Å}^{-3})$	$d\rho_0^{Tl}/dR\big|_{R=R_e}(\text{Å}^{-4})$
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[a] Experimental values taken from [12] have been corrected in light of an error pointed out in [13].

Cooke *et al.* did non-relativistic calculations....

Thallium iodine ($R_e = 2.8136$ Å): Benchmark calculations

Method	Basis	Hamiltonian	Approach	$\rho_0^{Tl}(\text{Å}^{-3})$	$d\rho_0^{Tl}/dR\big|_{R=R_e}(\text{Å}^{-4})$
HF	TZ2s1p	4C	$\langle \rho^{Tl} \rangle$	17347159.65	212.72
SAOP	TZ2s1p	4C	$\langle \rho^{Tl} \rangle$	17426852.47	120.26
CCSD(T)	TZ2s1p	4C	$\langle \rho^{Tl} \rangle$	17347293.64	142.43

Finite field CCSD(T) calculations. 30 electrons correlated (Tl: 5d6s6p + I:4d5s5p). Virtual cutoff: 36 a.u.

Only LL integrals included in the valence correlation
(with all integrals $d\rho^{Tl}/dR\big|_{R=R_e}$ changes by at most 1 Å^{-4}).

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Differential coefficient of the electron density from the function of the internuclear distance at the nucleus Pb or Tl, calculated
with the values of table 1

Molecule AB	$(d\rho/dR)^A_{R_e}$ (Å^{-4})	Molecule AB	$(d\rho/dR)^A_{R_e}$ (Å^{-4})
PbS	213(17)	TlF	254(30)
PbSe	177(15)	TlCl	185(25)
PbTe	148(11)	TlBr	142.0(42)
		TlI	120.6(38)

Note that CCSD(T) takes us away from the experimental result !

Nuclear volume correction to the rotational constant

The first-order change in the rotational constant due to a change of bond length is

$$B_e = \frac{\hbar}{2\mu R_e^2} \quad \Rightarrow \quad \delta B_e = -\frac{\hbar}{\mu R_e^3}\delta R_e = B_e \left(-\frac{2}{R_e}\right)\delta R_e$$

To determine the change in bond length due to a change of nuclear size of atom A, we consider the electronic energy as a function of internuclear distance R and nuclear radius ξ of atom A

$$E^{el} \equiv E^{el}(R, \xi)$$

The equilibrium bond length for given nuclear radius ξ is found by minimizing the energy with respect to internuclear distance

$$\left.\frac{dE^{el}}{dR}\right|_\xi = 0$$

The equilibrium distance accordingly becomes a function of internuclar distance $R_e \equiv R_e(\xi)$, and δR_e can be found by **variational perturbation theory**.

Nuclear volume correction to the equilibrium bond distance

$$\frac{dE^{el}}{dR}\bigg|_{\xi} = 0 \quad \Rightarrow \quad \frac{d^2E^{el}}{d\xi dR}\bigg|_{\xi_A} = \left[\frac{d^2E^{el}}{dR^2}\frac{dR}{d\xi} + \frac{\partial}{\partial\xi}\left(\frac{dE^{el}}{dR}\right)\right]_{\xi_A} = 0$$

$$\left[\frac{d^2E^{el}}{dR^2}\right]_{\xi_A} = k_e^A \quad \text{force constant for reference isotope A}$$

The electrostatic interaction of the electrons with nucleus A
depends on nuclear radius ξ of atom A

$$\frac{\partial}{\partial\xi}\left(\frac{dE^{el}}{dR}\right) = \frac{\partial}{\partial\xi}\frac{d}{dR}\left[\int \rho_e\left(\boldsymbol{r}_e; R, \xi\right)\phi_n^A\left(\boldsymbol{r}_e; \xi\right)d^3r_e\right]$$

$$\approx \int \frac{d\rho_e\left(\boldsymbol{r}_e; R\right)}{dR}\frac{\partial\phi_n^A\left(\boldsymbol{r}_e; \xi\right)}{d\xi}d^3r_e$$

$$\approx \frac{d\overline{\rho}_e}{dR}\int \frac{\partial\phi_n^A\left(\boldsymbol{r}_e; \xi\right)}{d\xi}d^3r_e$$

(we ignore any modification of ρ_e due to a change of nuclear size)

Nuclear models

In the relativistic domain a finite nucleus model is mandatory due to the singularity of the electronic wave function at a point nucleus

Homogeneously charged sphere

$$\rho_n^H\left(\boldsymbol{r}\right) = \rho_0^H \Theta\left(\zeta - r\right)$$

$$\frac{\partial \phi_n^H}{\partial \xi} = \begin{cases} -\frac{3Z}{2\xi^2}\frac{1}{4\pi\varepsilon_0}\left(1 - \frac{r^2}{\xi^2}\right) & ; \quad r \leq \xi \\ 0 & ; \quad r > \xi \end{cases}$$

Gaussian charge distribution

$$\rho_n^G\left(\boldsymbol{r}\right) = \rho_0^G \exp\left[-r^2/\xi_G^2\right]$$

$$\frac{\partial \phi_n^G}{\partial \xi} = -\frac{Z}{2\varepsilon_0}\xi_G\left(\frac{\partial \xi_G}{\partial \xi}\right)\rho_n^G$$

Connecting radii:

$$\left\langle r_n^2 \right\rangle = \frac{3}{5}\xi^2 = \frac{3}{2}\xi_G^2 \quad \Rightarrow \quad \xi_G = \xi\sqrt{\frac{2}{5}}$$

Both models then give the same result:

$$\left[\frac{\partial}{\partial \xi}\left(\frac{dE^{el}}{dR}\right)\right]_{\xi_A} \approx \frac{d\overline{\rho}_e}{dR}\int \left.\frac{\partial \phi_n^A\left(\boldsymbol{r}_e; \xi\right)}{\partial \xi}\right|_{\xi_A} d^3r_e = -\frac{4\pi}{5}Z_A\xi_A\frac{d\overline{\rho}_e}{dR}$$

Nuclear volume correction to the rotational constant

Change in equilibrium distance due to isotope substitution $A \to A'$

$$\delta R_e = -\frac{Z_A e^2}{6\varepsilon_0 k_e^A} \delta \left\langle r_n^2 \right\rangle_{AA'} \left(\frac{d\overline{\rho}_e}{dR}\right)_{R_e^A}$$

Using literature data we find for Tll
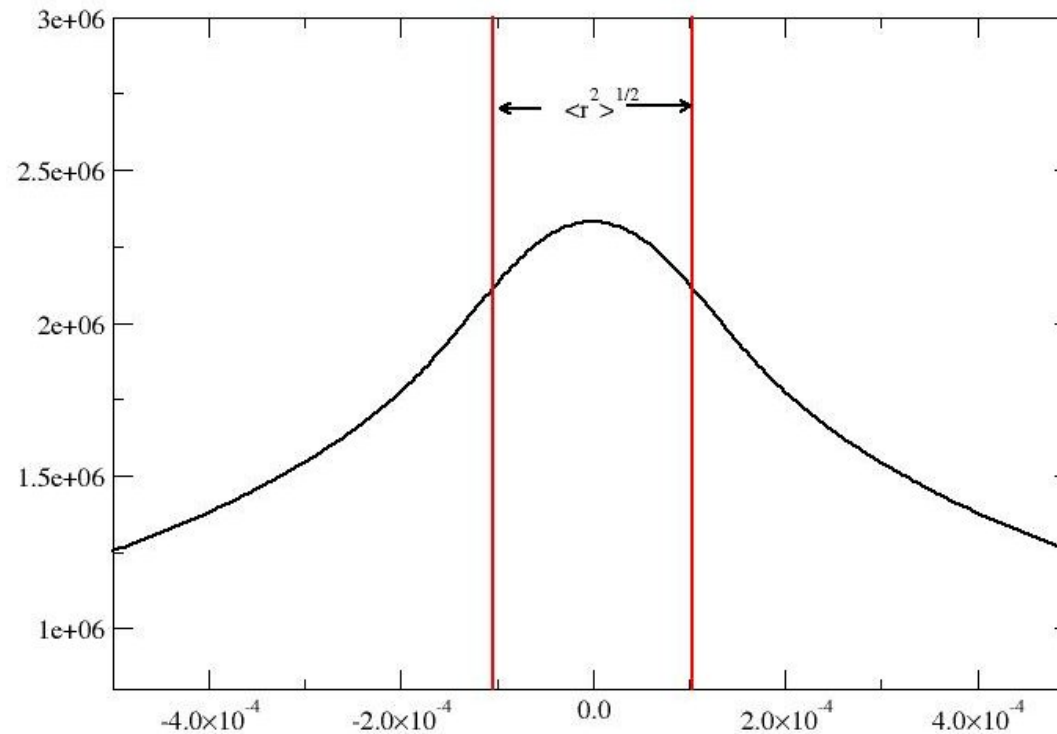
$$\delta R_e^{Tl(203,205)} = -6.4 \cdot 10^{-17} m \,!$$

Corresponding change in rotational constant

$$\delta B_e = B_e^A \left(-\frac{2}{R_e}\right) \delta R_e = B_e^A V_{01}^A \delta \left\langle r_n^2 \right\rangle_{AA'}; \quad V_{01}^A = \frac{Z_A e^2}{3\varepsilon_0 k_e^A R_e^A} \left(\frac{d\overline{\rho}_e}{dR}\right)_{R_e^A}$$

From effective to contact density

Since the effective density is sampled inside the nuclear volume it is typically approximated by the contact density, that is, value of the electronic density at the nucleus
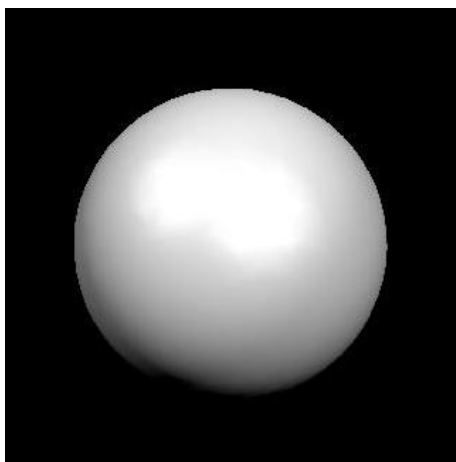
$$\bar{\rho} \approx \rho(0)$$

Is the contact density a good approximation to the effective density for heavy elements ?
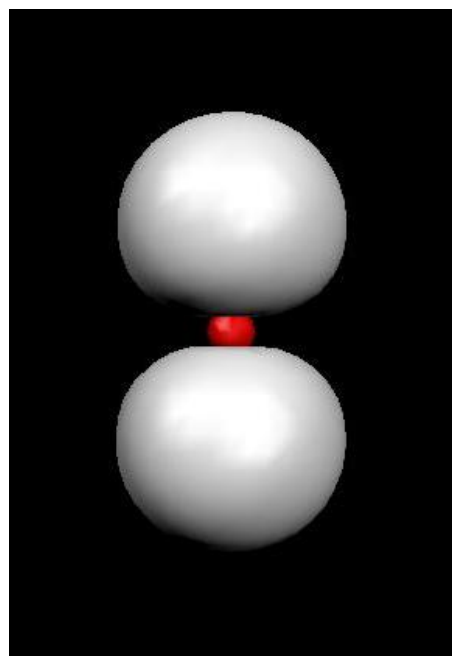
B. Fricke B and J. T. Waber, Phys Rev B **5** (1972) 3445

Relativistic atomic orbitals

$$\psi^{\mathrm{NR}}(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi) \Rightarrow \psi^{\mathrm{R}}(r,\theta,\phi) = \left[\begin{array}{c} R^L(r)\chi_{\kappa,m_j}(\theta,\phi) \\ iR^S(r)\chi_{-\kappa,m_j}(\theta,\phi) \end{array} \right]$$

	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$
j	1/2	1/2	3/2	3/2	5/2
κ	-1	+1	-2	+2	-3

$2(s,p)_{1/2,1/2}$

(z-axis anywhere)

$2(p,d)_{3/2,1/2}$

(z-axis in plane)
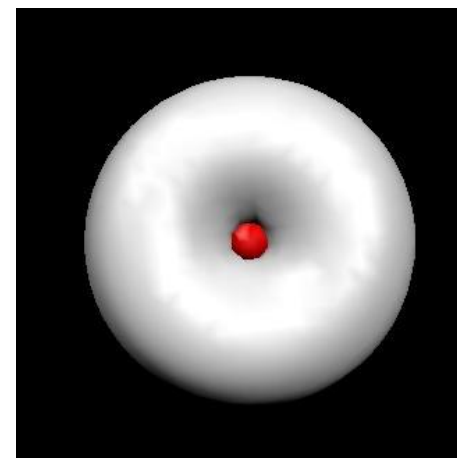
$2(p,d)_{3/2,3/2}$

(z-axis out of plane)

Atomic contact density

$$\rho^{Hg}(0) = \sum_i \left\langle \psi_i^{Hg} \left| \delta(\boldsymbol{r}) \right| \psi_i^{Hg} \right\rangle$$

$$= \sum_i \left[\left\langle R_i^L \left| \frac{\delta(r)}{4\pi r^2} \right| R_i^L \right\rangle_r \left\langle \chi_{\kappa,m} \mid \chi_{\kappa,m} \right\rangle_{(\theta,\phi)} + \right.$$

$$\left. + \left\langle R_i^S \left| \frac{\delta(r)}{4\pi r^2} \right| R_i^S \right\rangle_r \left\langle \chi_{-\kappa,m} \mid \chi_{-\kappa,m} \right\rangle_{(\theta,\phi)} \right]$$

$$= \frac{1}{4\pi} \sum_i \left[R_i^L(0) R_i^L(0) + R_i^S(0) R_i^S(0) \right]$$

Let us look at small r solutions of relativistic atomic orbitals

Small r solutions

- We consider radial solutions at small r:

$$R^L = r^{\gamma-1}\left(p_0 + p_1 r + p_2 r^2 + \ldots\right)$$

$$R^S = r^{\gamma-1}\left(q_0 + q_1 r + q_2 r^2 + \ldots\right)$$

- Point nucleus: $\gamma = +\sqrt{\kappa^2 - Z^2/c^2} < |\kappa|$ (singularity at the nucleus for $|\kappa| = 1$)

- Extended nuclei: $\gamma = |\kappa|$

  - $\kappa < 0$: $q_0 = p_1 = 0$ (for $s_{1/2}$- orbitals $(\kappa = -1)$ $R^L(0) = p_0$ and $R^S(0) = 0$)
  - $\kappa > 0$: $p_0 = q_1 = 0$ (for $p_{1/2}$- orbitals $(\kappa = 1)$ $R^L(0) = 0$ and $R^S(0) = q_0$)

In the relativistic case the contact density has contributions from the large components of $s_{1/2}$ orbitals <u>and</u> the small components of $p_{1/2}$ components.

- Non-relativistic case: $R(r) = r^l\left(a_0 + a_1 r + a_2 r^2 + \ldots\right)$

(a_1 is zero for extended nuclei, thus removing the cusp)

Contact vs. effective density

Orbital contributions for thallium atom (HF/TZ2s1p). All values are in atomic units a_0^{-3}.

	$\rho_e(0)$	$\bar{\rho}_e - \rho_e(0)$
$1s_{1/2}$	2112536.88	-215363.37
$2s_{1/2}$	322388.19	-33035.87
$3s_{1/2}$	74350.56	-7625.34
$4s_{1/2}$	18799.34	-1928.44
$5s_{1/2}$	3695.82	-379.14
$6s_{1/2}$	371.46	-38.11
$2p_{1/2}$	24695.53	-2449.09
$2p_{3/2}$	0	2 x 0.56
$3p_{1/2}$	6395.44	-634.80
$3p_{3/2}$	0	2 x 0.16
$4p_{1/2}$	1598.33	-158.67
$4p_{3/2}$	0	2 x 0.08
$5p_{1/2}$	280.27	-27.82
$5p_{3/2}$	0	2 x 0.01
$6p_{1/2}$	2.46	-0.24
$6p_{3/2}$	0	< 0.01
Total	2565114.28	-261639.27

Contact vs. effective density gradient

Effective and contact electron density gradients, respectively, at the nuclei Tl, Pb, and Pt calculated at the four-component Dirac-Coulomb level using the TZ2s+1p basis. The derivatives (in Å^{-4}) are taken at the respective experimental geometries of TlI, PbTe, and PtSi.

Method	$\rho_0^{[1]X}$	$\bar{\rho}^{[1]X}$	$\Delta(\bar{\rho}^{[1]X} - \rho_0^{[1]X})$
		TlI	
HF	212.15	190.29	**-10.3%**
DFT/PBE	114.53	102.67	**-10.4%**
DFT/SAOP	119.96	107.60	**-10.3%**
		PbTe	
HF	240.18	215.00	**-10.5%**
DFT/PBE	155.74	139.29	**-10.6%**
		PtSi	
HF	-1183.83	-1070.52	**-9.6%**
DFT/PBE	-656.39	-593.34	**-9.6%**

Final results

method	Hamiltonian	$\rho^{[1]X}$	V^X
		TlI	
experiment		120.6(38)	3.20(10)
DFT/SAOP	NR	21.09	0.57
CCSD(T)	^{4c}DC**	142.26	3.81
DFT/SAOP (Cooke)	(ZORA)	21.1	0.61^d
		PbTe	
experiment		148(11)	2.12(16)
DFT/SAOP	NR	19.64	0.28
CCSD(T)	^{4c}DC**	163.19	2.36
DFT/SAOP (Cooke)	(ZORA)	21.1	0.33^d
		PtSi	
experiment[C]^e			-0.72(12)
DFT/SAOP	NR	-135.64	-1.14
CCSD(T)	^{4c}DC**	-599.83	-5.05
DFT/SAOP (Cooke)	(ZORA)	-136.5	-1.10

All contact density results should be scaled down by 10%

Conclusions and perspectives

- The effects of nuclear size can be observed in high-resolution rovibrational spectroscopy of diatomics of heavy atoms

- 4-component relativistic calibration studies show a curious coincidence of error in previous experiemental and computational studies

- High accuray work should employ the effective rather than the contact density

- Future work is to investigate the effect of nuclear size on vibrational constant

- `http://dirac.chem.vu.nl`