Quantum chemistry for fundamental physics

From the Standard Model to molecular structure theory

Konstantin Gaul

Helmholtz Institut Mainz
Johannes Gutenberg-Universitiät Mainz, Germany

Search for new physics with low-energy precision tests, UG summer school, June 29 to July 4 2025

The plan

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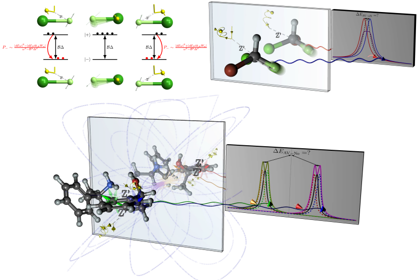
Today:
From the Standard Model to molecular structure theory

- Standard Model of particle physics, cosmology and beyond
- A crash course in relativistic molecular structure

Parity violation

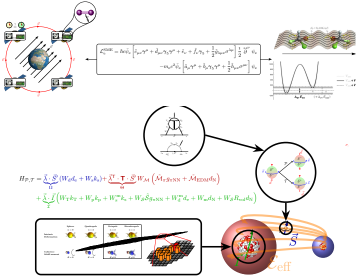
Rovibrational spectroscopy



NMR spectroscopy

Thursday:
Molecular probes of New Physics

- Molecular parity violation within and beyond the Standard Model
- Lorentz invariance violation
- New bosons/fifth force
- Electric dipole moments in atoms and molecules



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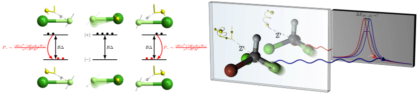

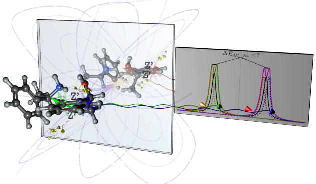

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From the Standard Model to molecular structure theory

The Standard Models of particle physics, cosmology and beyond

Force	rel. Strength	Range/m	Mediator
Gravity	1×10^{-43}	∞	graviton?
Weak	1×10^{-14}	1×10^{-18}	W and Z
Electromagnetic	1×10^{-3}	∞	photon
Strong	1	1×10^{-15}	gluon

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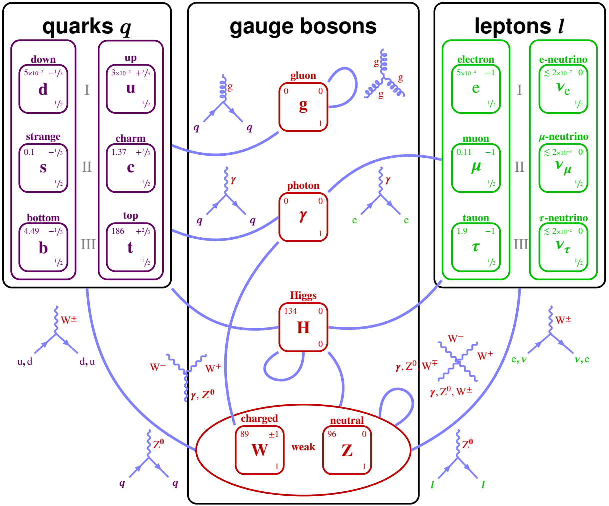
- Standard Model (Quantum field theory)
  - Standard electroweak theory
    - ★ Quantum electrodynamcis
    - ★ Fermi's theory of weak interactions
  - Quantum chromodynamics
- General relativity

Standard model of particle physics



Symmetry	Conserved quantity	Non-observable	SM
	Continuous symmetries		
translation in time	energy	absolute time	✓
translation in space	linear momentum	absolute spatial position	✓
rotation	angular momentum	absoulte spatial direction	✓
Lorentz symmetry	$\mathcal{CPT}$	absolute velocity	✓
	Discrete symmetries		
permutation symmetry	Bose-Einstein/Fermi-Dirac statistics	difference between identical particles	✓
inversion in space	parity ($\mathcal{P}$)	absolute left/right	✗
inversion in time	time-reversal ($\mathcal{T}$)	absolute direction of time	✗
inversion of electric charge	charge conjugation ($\mathcal{C}$)	absolute sign of electric charge	✗
	Unitary symmetries		
$U(1)$ gauge invariance	electric charge Q	phase shifts between states of different Q	✓
$SU_\mathrm{L}(2)$ gauge invariance	weak charge Q_W	phase shifts between states of different Q_W	✓
$SU(3)$ gauge invariance	color charge Q_c	phase shifts between states of different Q_c	✓

T. D. Lee, Particle Physics and Introduction to Field Theory, Harwood Academic Publishers, Chur, Switzerland, **1981**.

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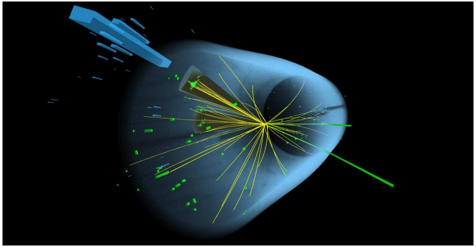
- The Standard Model agrees with experimental data to highest precision in history of physics!
- Prediction of W, Z, g, t, c... and Higgs boson!

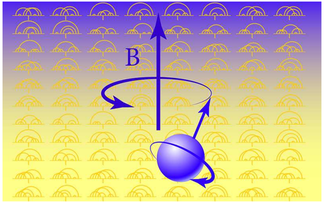


CERN

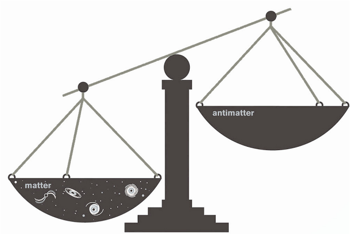
- Most precise predictions in QED
  - Anomalous magnetic dipole moment of the electron $a_\mathrm{e} = (g-2)/2$:

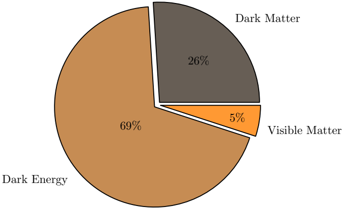
$$a_\mathrm{e}(\mathrm{exp}) = 0.00115965218059(13)$$
$$a_\mathrm{e}(\mathrm{theo}) = 0.00115965218178(77)$$

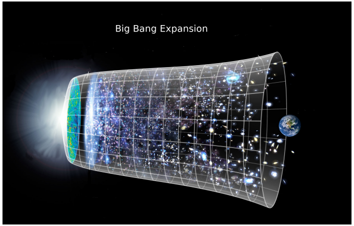
    1 part in 10^{12} agreement!
  - Other magnetic dipole moments (muon, tauon, etc.)
  - Lifetime of muon
  - Many more...



T. Aoyama et al., *Phys. Rev. Lett.* **2012**, *109*, 111807, X. Fan et al., *Phys. Rev. Lett.* **2023**, *130*, 071801.







Unexplained phenomena:

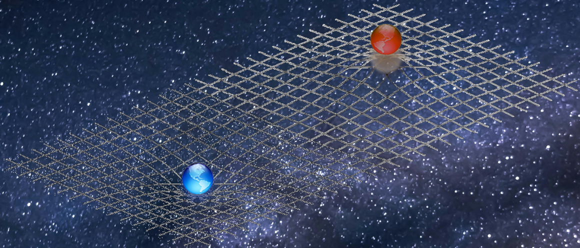
- Gravity
- Dark matter and dark energy (Standard Model of cosmology)
- Inflation (flatness and isotropy of the universe)
- Baryonasymmetry (imbalance of matter and antimatter in the observed universe)
- Neutrino oscillations (extension of the Standard Model)

"Discrepancies":

"Neutron lifetime puzzle", B meson decay, missing hadrons and "glueballs", sterile neutrinos, muon-μ, proton radius

Theoretical/conceptual "problems":

Empirical formulas (Koide, CKM mixing matrix, masses and Higgs vacuum expectation value), solving QCD, hierachy problem, number of parameters (19/28), quantum triviality, strong $C\mathcal{P}$ "problem", etc.



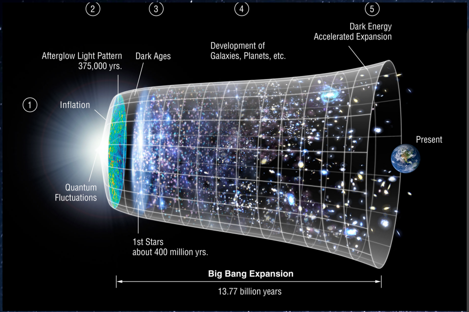
“Size of curvature”

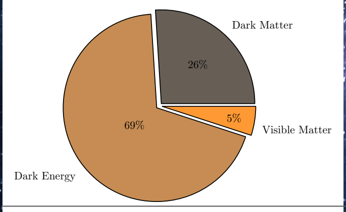
Measure of deformation along shortest path → $$\boxed{R_{\mu\nu} - \frac{1}{2} R g_{\mu\nu} = 8\pi G T_{\mu\nu}}$$ ← energy/momentum density and flux

Metric tensor

⇒ Gravity is a **pseudo-force**

https://commons.wikimedia.org/wiki/File:One-sided_spacetime_curvatures.png

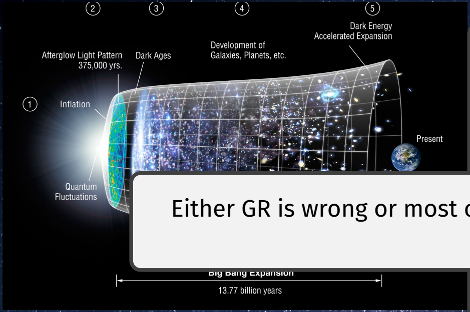


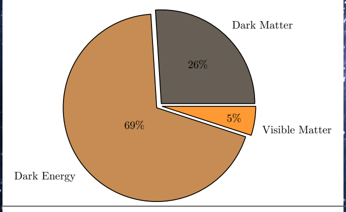


NASA/WMAPscienceteam

- In GR **absolute energy** matters!
- Constant vacuum energy density ρ_{vac} adds to $T_{\mu\nu}$
- $\Lambda = \frac{\rho_{\text{vac}}}{8\pi G}$ is the cosmological constant
- Our universe is fairly flat and matter dominated: $1 - \Omega_{\text{c}} \approx \Omega_\Lambda + \Omega_{\text{M}}$
- From the Friedmann equation[a]
- Matter- (M), radiation- (R) and vacuum (Λ) density parameters today: $\Omega_\Lambda \propto \Omega_c a^2 \propto \Omega_{\text{M}} a^3 \propto \Omega_{\text{M}} a^4$
- Observation $\Omega_c \approx 0$, $\Omega_{\text{M}} = 0.3 \pm 0.1$, $\Omega_\Lambda = 0.7 \pm 0.01$
  $\leftrightarrow$ Best estimates of baryon density $\Omega_{\text{b}} = 0.04 \pm 0.02$!

[a] S. M. Carroll, Spacetime and Geometry: An Introduction to General Relativity, Cambridge University Press, **2019**.





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Either GR is wrong or most of the matter content of the universe is dark!

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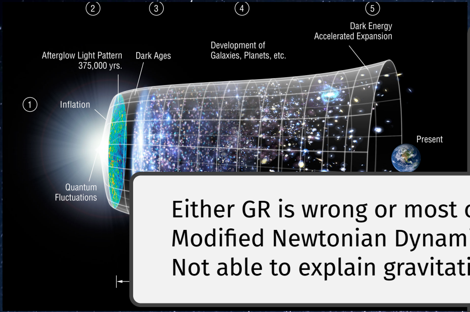

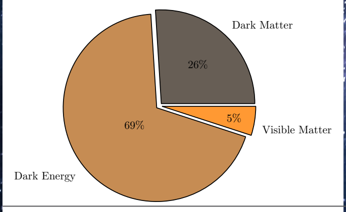

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Modified Newtonian Dynamics (MOND)? $\rightarrow$
Not able to explain gravitational lensing, waves…

ty
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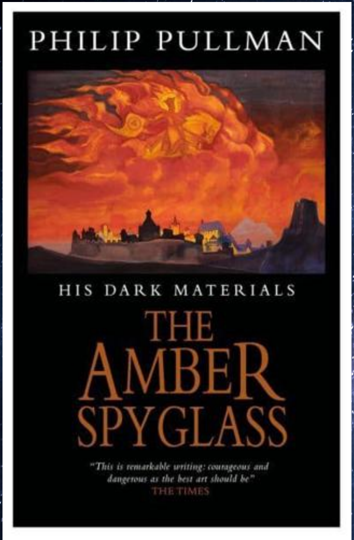
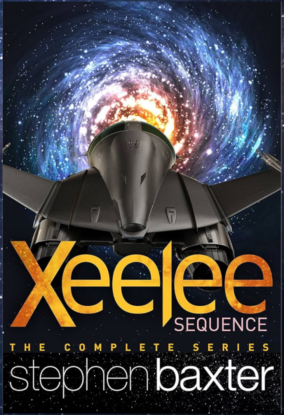
What is dark matter?

The Standard Models of particle physics, cosmology and beyond

Dark matter in science-fiction



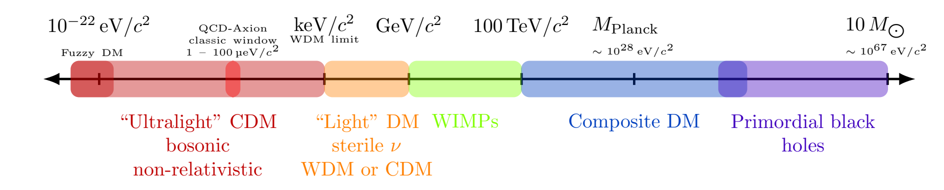
"Shadows are particles of consciousness. You ever heard anything so stupid? No wonder we can't get our grant renewed... And here goes the crazy part: you can't see them unless you expect to. Unless you put your mind in a certain state." —Mary Melone (Dark matter research unit, Oxford) in "The amber spyglass" by Philip Pullman



Dark matter creatures...
They might tell us what they are made of?

The Standard Models of particle physics, cosmology and beyond

Dark matter in science ~~fiction~~



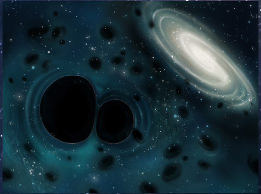
Pseudoscalar bosons for solving strong $\mathcal{CP}$ problem

$$\theta \frac{g_s^2}{32\pi^2} \tilde{G}_a^{\mu\nu} G^a_{\mu\nu}$$

(Weinberg and Wilczek)

Many low-energy searches: **axion-electric effect** (light through wall) or the **axion-wind** (magnetic field sensing)

Primordial black holes (MACHOs)



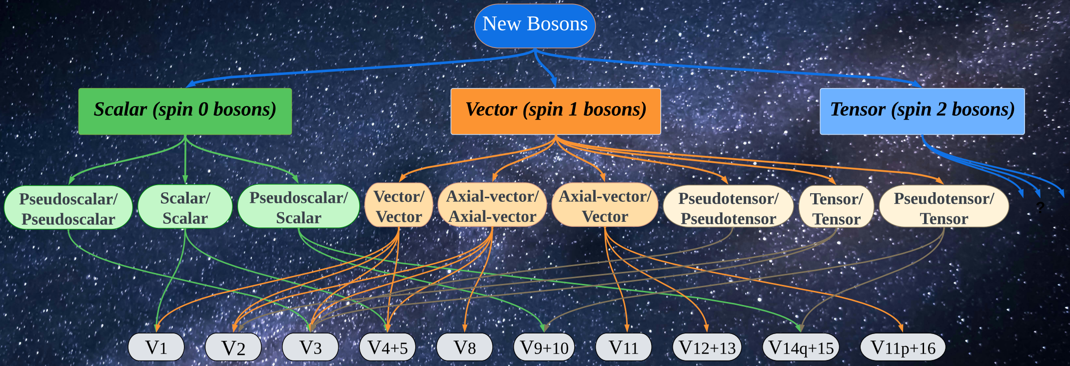
Zel'dovich, Nowikow and later Hawking

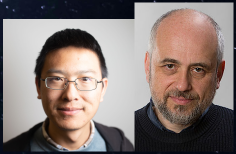
Formed shortly after big bang (before stars!)

Masses down to 10^{12} m ⇔ size of a fm!

The Standard Models of particle physics, cosmology and beyond

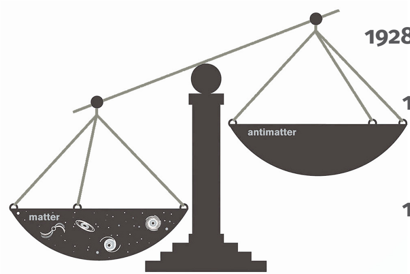
New bosons?





L. Cong et al., *Rev. Mod. Phys.* **2025**, 97, 025005

Why is there matter at all?



https://www.symmetrymagazine.org/article/october-2005/explain-it-in-60-seconds

1928/32 Feynman–Stückelberg interpretation of Dirac equation $\rightarrow$ Antimatter

1933 Discovery of the positron by Anderson.

Where is the antimatter?

Hidden anti-matter clusters? $\rightarrow N_{\mathrm{anti}}/N_{\mathrm{mat}} < 10^{-6}$!

1967 Sakharov conditions

1. Baryon number (B) violation ΔB,
2. C- and $C\mathcal{P}$-violation,
3. Deviation from thermal equilibrium.

A. D. Sakharov, *JETP Lett.* **1967**, *5*, 24, A. D. Sakharov, *Sov. Phys. Usp.* **1991**, *34*, 392–393.
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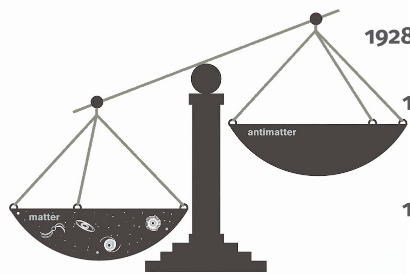

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✓$\mathcal{C}$ **is maximally violated in the SM** (electroweak)
✓$\mathcal{CP}$ **is violated in the SM** (CKM, neutrino oscillations)
✓B **is violated in the SM** (non-perturbative, electroweak)
✓**Primordial plasma** was out of equilibrium in the **expanding universe**

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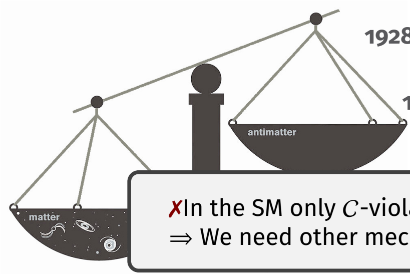

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Where is the antimatter?

✗In the SM only C-violation is sufficient!
$\Rightarrow$ We need other mechanisms for $C\mathcal{P}$ and B violation!

3. Deviation from thermal equilibrium.

✓C **is maximally violated in the SM** (electroweak)
✓$C\mathcal{P}$ **is violated in the SM** (CKM, neutrino oscillations)
✓B **is violated in the SM** (non-perturbative, electroweak)
✓**Primordial plasma** was out of equilibrium in the **expanding universe**
✗$C\mathcal{P}$-violation very small in the SM (Jarlskog invariant $\sim 10^{-5}$)
✗B-violation minuscule (sphalerons, at $T = 0$: $\Gamma/V \sim m_W^4 \exp(-8\pi^2/g^2) \sim m_W^4 10^{-180}$)

A. D. Sakharov, *JETP Lett.* **1967**, *5*, 24, A. D. Sakharov, *Sov. Phys. Usp.* **1991**, *34*, 392–393.
L. Canetti et al., *New J. Phys.* **2012**, *14*, 095012.
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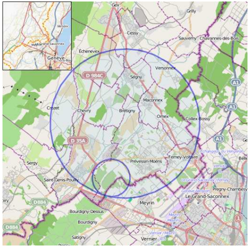
Searching for New Physics at different scales

Searching for New Physics at different scales

Astrophysics

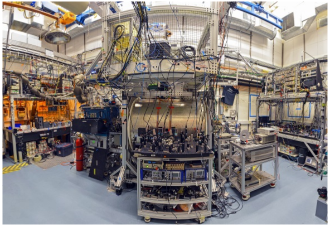
https://www.eso.org/public/germany/images/potw1604a/

High-energy physics



CERN: https://home.cern/resources/image/accelerators/lhc-images-gallery

Low-energy precision tests



ACME Collaboration: http://www.electronedm.org/

https://first-tf.fr/grand-public-scolaires/ressources-grand-public/

1. Precise comparison of theory and experiment

- ✓ Small well controllable systems: H,D,He,HD,H_2 etc.
- ✓ Accuracy of calculations $\ll 1\%$
- ✗ System selection usually limited by nuclear structure

2. Looking for non-observables of the SM

- ✓ Symmetry violation beyond the Standard Model
- ✓ Forbidden transitions in atoms and molecules
- ✓ Measuring very precisely zero
- ✓ Weakly dependent on theory uncertainty
- ✗ Very important to control experimental systematics

REVIEWS OF MODERN PHYSICS, VOLUME 90, APRIL–JUNE 2018

Search for new physics with atoms and molecules

M.S. Safronova[1,2], D. Budker[3,4,5], D. DeMille[6], Derek F. Jackson Kimball[7], A. Derevianko[8] and Charles W. Clark[2]

Searching for New Physics at different scales

How to do a low-energy precision test: Two strategies

1. Precise comparison of theory and experiment

- ✓ Small well controllable systems: H,D,He,HD,H_2 etc.
- ✓ Accuracy of calculations $\ll 1\%$
- ✗ System selection usually limited by nuclear structure

2. Looking for non-observables of the SM

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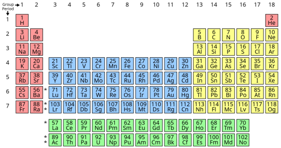
We will follow the second route!

Searches for $\mathcal{P}$-violation, $\mathcal{CP}/\mathcal{P},\mathcal{T}$-violation, $\mathcal{P}$-violating dark matter, local Lorenz invariance violations, variations of fundamental constants, etc…

Searching for New Physics at different scales

why molecules?

Pro	Contra
✓Complex many body system	✗Complex many body system
✓Internally broken symmetries	✗Lower resolution than in atoms
✓Nucleus-nucleus interactions	✗Ab initio description can be limited
✓Can have simpler electronic structure than atoms	
✓Recent breakthroughs in molecular spectroscopy	



- Computational limitations come most often from the nucleus.
- Experimental limitations can be outrivaled by internal enhancement mechanisms.

⇒ Tailoring a tuned quantum sensor from the periodic table!

A crash course in relativistic molecular structure

Molecules are composed of electrons and nuclei
✓In good approximation only electromagnetic force matters!

G. A. Aucar, *Phys. Chem. Chem. Phys.* **2014**, *16*, 4420–4438.
K. G. Dyall, *J. Chem. Phys.* **1997**, *106*, 9618–9626, M. Reiher, A. Wolf, Relativistic Quantum Chemistry, John Wiley & Sons, Ltd, **2014**.

Molecules are composed of electrons and nuclei

✓In good approximation only electromagnetic force matters!

$$\mathcal{L}_{\text{QED}} = \underbrace{-\frac{1}{4}F_{\mu\nu}F^{\mu\nu}}_{\mathcal{L}_{\text{photon}}} + \sum_i \bar{\psi}_i \left[\underbrace{\mathrm{i}\hbar c\gamma^\mu \partial_\mu \psi_i}_{\mathcal{L}_{\text{kin}}} \underbrace{-m_i c^2}_{\mathcal{L}_{\text{mass}}} \underbrace{-q_i c\gamma^\mu A^\mu}_{\mathcal{L}_{\text{int}}} \right] \psi_i$$

$$\mu = 0, 1, 2, 3;\ x_\mu = (ct, x, y, z)_\mu;\ \partial^\mu = \frac{\partial}{\partial x_\mu};$$

$$A^\mu = [(\phi, -A_x, -A_y, -A_z)^\mathsf{T}]_\mu;\ F_{\mu\nu} = \begin{pmatrix} 0 & \mathcal{E}_x/c & \mathcal{E}_y/c & \mathcal{E}_z/c \\ -\mathcal{E}_x/c & 0 & -\mathcal{B}_z & \mathcal{B}_y \\ -\mathcal{E}_y/c & \mathcal{B}_z & 0 & -\mathcal{B}_x \\ -\mathcal{E}_z/c & -\mathcal{B}_y & -\mathcal{B}_x & 0 \end{pmatrix}_{\mu\nu}$$

$$\boldsymbol{\gamma}^0 = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix};\boldsymbol{\gamma}^k = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}^k \\ -\boldsymbol{\sigma}^k & \mathbf{0} \end{pmatrix};\ \boldsymbol{\gamma}^5 = \mathrm{i}\boldsymbol{\gamma}^0\boldsymbol{\gamma}^1\boldsymbol{\gamma}^2\boldsymbol{\gamma}^3;\ \boldsymbol{\beta} = \boldsymbol{\gamma}^0;\ \vec{\boldsymbol{\alpha}} = \boldsymbol{\gamma}^0\vec{\boldsymbol{\gamma}};\ \vec{\boldsymbol{\Sigma}} = \boldsymbol{\gamma}^0\boldsymbol{\gamma}^5\vec{\boldsymbol{\gamma}}$$

G. A. Aucar, *Phys. Chem. Chem. Phys.* **2014**, *16*, 4420–4438.

K. G. Dyall, *J. Chem. Phys.* **1997**, *106*, 9618–9626, M. Reiher, A. Wolf, Relativistic Quantum Chemistry, John Wiley & Sons, Ltd, **2014**.

Molecules are composed of electrons and nuclei
✓In good approximation only electromagnetic force matters!

$$\mu = 0, 1, 2, 3;\ x_\mu = (ct, x, y, z)_\mu;\ \partial^\mu = \frac{\partial}{\partial x_\mu};$$

$$\mathcal{L}_{\text{QED}} = \underbrace{-\frac{1}{4} F_{\mu\nu} F^{\mu\nu}}_{\mathcal{L}_{\text{photon}}} + \sum_i \bar{\psi}_i \left[\underbrace{\mathrm{i}\hbar c \gamma^\mu \partial_\mu \psi_i}_{\mathcal{L}_{\text{kin}}} \underbrace{- m_i c^2}_{\mathcal{L}_{\text{mass}}} \underbrace{- q_i c \gamma^\mu A^\mu}_{\mathcal{L}_{\text{int}}} \right] \psi_i$$

$$A^\mu = [(\phi, -A_x, -A_y, -A_z)^\mathsf{T}]_\mu;\ F_{\mu\nu} = \begin{pmatrix} 0 & \mathcal{E}_x/c & \mathcal{E}_y/c & \mathcal{E}_z/c \\ -\mathcal{E}_x/c & 0 & -\mathcal{B}_z & \mathcal{B}_y \\ -\mathcal{E}_y/c & \mathcal{B}_z & 0 & -\mathcal{B}_x \\ -\mathcal{E}_z/c & -\mathcal{B}_y & -\mathcal{B}_x & 0 \end{pmatrix}_{\mu\nu}$$

$$\gamma^0 = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}; \gamma^k = \begin{pmatrix} \mathbf{0} & \sigma^k \\ -\sigma^k & \mathbf{0} \end{pmatrix}; \gamma^5 = \mathrm{i}\gamma^0\gamma^1\gamma^2\gamma^3;\ \boldsymbol{\beta} = \gamma^0;\ \vec{\alpha} = \gamma^0\vec{\gamma};\ \vec{\boldsymbol{\Sigma}} = \gamma^0\gamma^5\vec{\gamma}$$

- ✗ Interaction term is **particle field dependent**! → Many-body problem is tough in QED (For **two** particles: **Bethe-Salpeter equation**)
- ✗ Combination of electron correlation and QED an open problem (how to treat virtual positronic states?)!

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- ✓ Fortunately: QED is perturbative!

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$$\mu = 0,1,2,3;\ x_\mu = (ct, x, y, z)_\mu;\ \partial^\mu = \frac{\partial}{\partial x_\mu};$$

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$$\gamma^0 = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}; \gamma^k = \begin{pmatrix} \mathbf{0} & \sigma^k \\ -\sigma^k & \mathbf{0} \end{pmatrix}; \gamma^5 = i\gamma^0\gamma^1\gamma^2\gamma^3;\ \beta = \gamma^0;\ \vec{\alpha} = \gamma^0\vec{\gamma};\ \vec{\Sigma} = \gamma^0\gamma^5\vec{\gamma}$$

- ✗ Interaction term is **particle field dependent**! ⟶ Many-body problem is tough in QED (For **two** particles: **Bethe-Salpeter equation**)
- ✗ Combination of electron correlation and QED an open problem (how to treat virtual positronic states?)!
- ✓ Fortunately: QED is perturbative!
- ✓ Common approximations:
  - "No-pair" approximation (Electron-positron pair creation at $\sim 1\,\text{MeV}$!)
  - Instantaneous interactions (classical Coulomb)
    ⟶ Perturbative QED correction from the photon field
  - Nuclei are hard spherical charges $eZ\rho(r)$
  - Electronic and nuclear motion is separated (Born–Oppenheimer approximation)
  - $\alpha \to \infty$ (non-relativistic limit) (Perturbation theory on the Schrödinger equation is predictive for $E \ll m_\text{e}c^2 \sim 511\,\text{keV}$)
  - Bound-state atomic/molecular Hamiltonians:

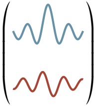
$$\hat{H} = c\vec{\alpha}\cdot\hat{\vec{p}} + \beta m_\text{e}c^2 + \hat{V}_\text{eN} + \hat{V}_\text{ee} + \hat{V}_\text{NN},\ \lim_{\alpha\to 0}\hat{H} - m_\text{e}c^2 = \hat{H}_\text{nr} = \frac{\hat{\vec{p}}^2}{2m_\text{e}} + \hat{V}_\text{eN} + \hat{V}_\text{ee} + \hat{V}_\text{NN}$$

G. A. Aucar, *Phys. Chem. Chem. Phys.* **2014**, *16*, 4420–4438.

K. G. Dyall, *J. Chem. Phys.* **1997**, *106*, 9618–9626, M. Reiher, A. Wolf, Relativistic Quantum Chemistry, John Wiley & Sons, Ltd, **2014**.

Time-independent Dirac/Schrödinger equation for a central Coulomb potential ($V_{\mathrm{eN}} = \frac{-eZ}{4\pi\epsilon_0 r}$ for $\rho(r) = 4\pi\delta(r)$):

$$\hat{H}\Psi_n = E_n\Psi_n$$

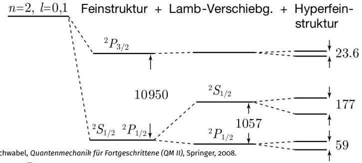
For Dirac $\Psi_n =$  $\otimes \begin{pmatrix} |\uparrow\rangle \\ |\downarrow\rangle \end{pmatrix}$ is a bi-spinor (four-vector)

"Large component" for electronic states
and "small component" for positronic states

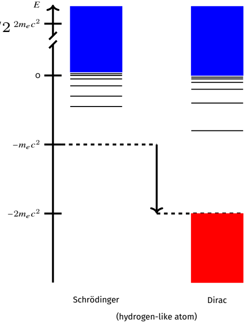
$$E_{n,j} = mc^2 \left[1 + \left(\frac{Z\alpha}{n - j - \frac{1}{2} + \underbrace{\sqrt{(j+\frac{1}{2})^2 - (Z\alpha)^2}}_{\text{Electronic Lorentz factor}}} \right)^2 \right]^{-1/2}$$

$$\lim_{\alpha \to 0} E_{n,j} - mc^2 = -\frac{mc^2 (Z\alpha)^2}{2n^2}$$

Shifting energies by mc^2 to obtain a non-relativistic analogue!
Dirac sea? ⟶ Negative energy states are empty!



Schwabel, *Quantenmechanik für Fortgeschrittene (QM II)*, Springer, 2008.



Relativistic effects? Paul Dirac's assessment

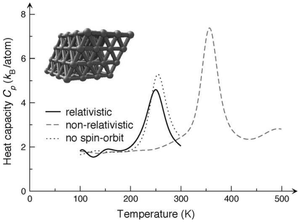
§ 1. *Introduction.*

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum

P. A. M. Dirac, *Proc. Roy. Soc. Lond. A* **1929**, *123*, 714–733.

Classics in chemistry:

- Why is gold so shiny-yellow? 

- Why does your (old) car start? 
- Why is mercury liquid at room temperature? 

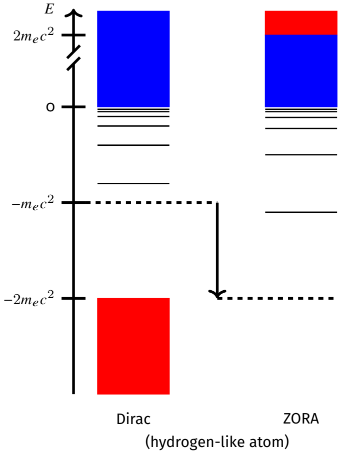
K. G. Dyall, K. Fægri, Jr., Introduction to Relativistic Quantum Chemistry, Oxford University Press, **2007**, N. E. Christensen, B. O. Seraphin, *Phys. Rev. B* **1971**, *4*, 3321–3344, P. Romaniello, P. L. de Boeij, *J. Chem. Phys.* **2005**, *122*, 164303, R. Ahuja et al., *Phys. Rev. Lett.* **2011**, *106*, 018301, F. Calvo et al., *Angew. Chem. Int. Ed.* **2013**, *52*, 7583–7585.

- Positronic states not populated in the molecule ⇒ implicit treatment of the small component!
- Elimination of the small component at the one-particle level:
  - Two-step approaches (elimination on the matrix level, RI): DKH, X2C
  - One-step approaches (elimination on the operator level): (Beit-)Pauli, ZORA

$$\begin{pmatrix} \hat{V} - \epsilon & c\vec{\boldsymbol{\sigma}} \cdot \hat{\vec{p}} \\ c\vec{\boldsymbol{\sigma}} \cdot \hat{\vec{p}} & \hat{V} - \epsilon - 2m_\mathrm{e}c^2 \end{pmatrix} \begin{pmatrix} \psi_\mathrm{L} \\ \psi_\mathrm{S} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\Rightarrow \psi_\mathrm{S} = \left(2m_\mathrm{e}c^2 - \hat{V} + \epsilon\right)^{-1} c\vec{\boldsymbol{\sigma}} \cdot \hat{\vec{p}}\psi_\mathrm{L}$$

- Expansion of $\left(2m_\mathrm{e}c^2 - \hat{V} + \epsilon\right)^{-1}$
  - Pauli: $\frac{1}{2m_\mathrm{e}c^2} \sum_{k=0}^{\infty} \left[\frac{\hat{V}-\epsilon}{2m_\mathrm{e}c^2}\right]^k$
  - Regular: $\frac{1}{2m_\mathrm{e}c^2-\hat{V}} \sum_{k=0}^{\infty} \left[\frac{-\epsilon}{2m_\mathrm{e}c^2-\hat{V}}\right]^k$ ⇒ ZORA: $\frac{1}{2m_\mathrm{e}c^2-\hat{V}}$
- ZORA usually captures all important relativistic effects for valence states!
- Core states can be renormalized (IORA)
- Missing two-electron effects usually negligible $\ll 1\%$ for heavy elements!



- Positro
  of the s
- Elimina
  - Two-ste
  - One-ste

Quantum electrodynamic corrections for molecules: Vacuum polarization and electron self-energy in a two-component relativistic framework

Kjell Janke ; Andrés Emilio Wedenig ; Peter Schwerdtfeger ; Konstantin Gaul ; Robert Berger

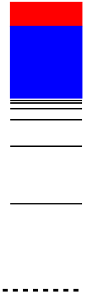
Check for updates

J. Chem. Phys. 162, 104111 (2025)
https://doi.org/10.1063/5.0252409

TABLE III. SE (Flambaum–Ginges) and VP (Uehling) contributions in eV to the $^2P_{1/2} \leftarrow {}^2S_{1/2}$ and $^2P_{3/2} \leftarrow {}^2S_{1/2}$ transitions calculated as expectation values based on ZORA-HF/dyall.cv3z calculations, using prefactor (6). A comparison[31] with four-component numerical DHF calculations with perturbative treatment of the QED contributions. *Z* is the nuclear charge and *N* is the number of electrons.

Z	N	$V_{\mathrm{SE,2P1/2}}$	Dev. (%)	$V_{\mathrm{SE,2P3/2}}$	Dev. (%)	$V_{\mathrm{VP,2P1/2}}$	Dev. (%)	$V_{\mathrm{VP,2P3/2}}$	Dev. (%)
10	3	-1.498×10^{-2}	0.0	-1.436×10^{-2}	0.0	7.643×10^{-4}	0.0	7.643×10^{-4}	0.0
20	3	-2.065×10^{-1}	0.5	-1.936×10^{-1}	0.0	1.414×10^{-2}	1.4[a]	1.417×10^{-2}	0.7[b]
30	3	-8.864×10^{-1}	0.1	-8.179×10^{-1}	0.1	7.562×10^{-2}	0.7	7.616×10^{-2}	0.7
40	3	-2.448	0.3	-2.238	0.4	2.526×10^{-1}	0.4	2.568×10^{-1}	0.4
50	3	-5.379	0.5	-4.906	0.6	6.631×10^{-1}	0.3	6.838×10^{-1}	0.2
60	3	-1.032×10^{1}	1.1	-9.467	1.0	1.513	0.1	1.591	0.3
70	3	-1.810×10^{1}	1.1	-1.691×10^{1}	1.3	3.169	0.4	3.420	0.6
80	3	-2.988×10^{1}	1.2	-2.885×10^{1}	1.6	6.293	0.5	7.040	0.9

- Expans
  - Pauli:
  - Regular



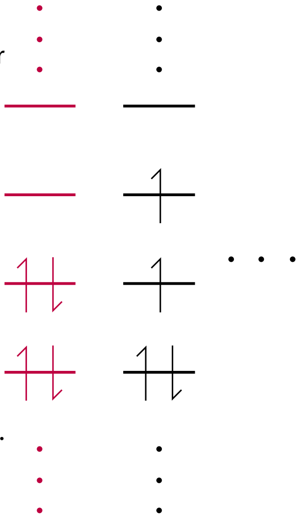
- ZORA usually captures all important relativistic effects for valence states!
- Core states can be renormalized (IORA)
- Missing two-electron effects usually negligible $\ll 1\%$ for heavy elements!

Many-electron wave function $\Psi(\vec{r}_1, \ldots, \vec{r}_N)$ must be totally anti-symmetric under exchange of two electrons (Spin-statistics theorem):

$$\Phi_j \sim \hat{\mathscr{A}} \prod_i \psi_{ij}(\vec{r}_i)$$ **Slater determinant**

Ψ_j does not need to be of structure Φ_j but it can be shown that for any Ψ_j:

$$\Psi_j = \sum_I c_{Ij} \Phi_I$$ **(Configuration Interaction),**



where the sum runs over all configurations Φ_I in the full single-particle space...
Number of determinants grows $\binom{M}{N}$ for N electrons and M one-particle functions.
$\Rightarrow$ Intractable problem for most atoms and molecules!

A. Szabo, N. S. Ostlund, Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory, Dover Publications, INC., Mineola, New York, **1996**, T. Helgaker et al., Molecular Electronic-Structure Theory, John Wiley & Sons, Ltd, **2000**.

Quantum chemistry ⇔ Obtaining the most efficient and accurate approximations to Ψ_j.

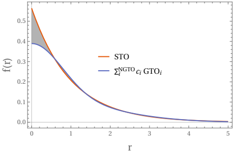
Approximating the one-particle space

Expand single-particle function ϕ_i in set of known functions $\{\chi_\mu\}$ inspired by H-atom solutions:

$$\chi_\mu(\vec{r}) = (x - X_\mu)^{l_{x\mu}} (y - Y_\mu)^{l_{y\mu}} (z - Z_\mu)^{l_{x\mu}} \times \exp\left(-\zeta_\mu \left|\vec{r} - \vec{R}_\mu\right|^k\right)$$

$$\phi_i(\vec{r}) = \sum_{\mu=1}^{M} C_{\mu i} \chi_\mu(\vec{r})$$

In most cases we choose $k = 2$ (Gaussian) for numerical simplicity. Closer to H-atom solution would be $k = 1$.



Approximating the N-particle space

$\Psi_j \approx \Phi_{j0}$, scales M^3
Hartree–Fock
$\min_{\phi_i} E[\Phi_{j0}(\{\phi_i\})]$

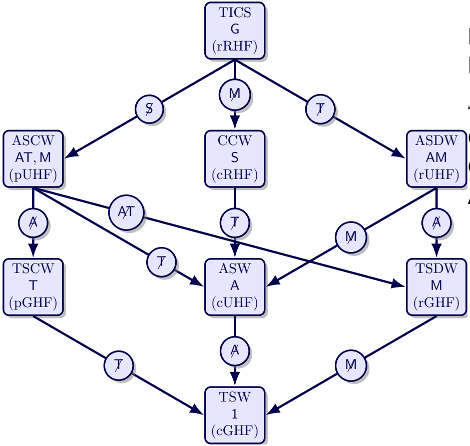
$\Psi_j \approx \sum_{I \in \mathcal{M}_K} \Phi_{jI}$, scales $\binom{N+K}{N}$
Multi-reference methods
MCSCF, CASSCF, RASSCF, DMRG,...
$\min_{\phi_i, \Phi_{jI}} E[\Phi_j(\{\phi_i\})]$

$\Psi_j \approx \sum_{k}^{N_{\mathrm{exc}}} \hat{T}_k \Phi_{j0}$, scales M^5-M^7,...
Single-reference correlated methods
CI,CC,MBPT,MPn,...
Not necessarily variational

$\Psi_j \approx \sum_{k}^{N_{\mathrm{exc}}} \hat{T}_k \tilde{\Psi}_j$; $\tilde{\Psi}_j \approx \sum_{I \in \mathcal{M}_K} \Phi_{jI}$
Multi-reference correlated methods
MRCI, MRCC, CASPTn, GASCI, FSCC,...

$\Psi_j \approx \sum_I \Phi_{jI}$
Full CI
exact diagonaliztion

We can obtain mixed electronic configuration by breaking the symmetry of the Hamiltonian (Löwdin symmetry dilemma):



Hamiltonian invariant under T = $\{-\mathbf{1}, \mathbf{1}, -\hat{\Theta}, \hat{\Theta}\}$
Non-relativistic Hamiltonian additionally invariant under $\hat{K}$ & $s(\vec{n},\theta) = \exp\left(\imath \frac{\theta}{2} n_i \boldsymbol{\sigma}^i\right)$ S = $\{s(\vec{n},\theta) : \vec{n} = \mathbb{R}^3, ||\vec{n}|| = 1, \theta \in \{0, 4\pi\}\}$
G = S ⊗ T , has eight subgroups:
G, S, T, A($\vec{n}$) = $\{s(\vec{n},\theta) : \theta \in \{0,4\pi\}\}$, M($\vec{n}$) = $\{\mathbf{1}, \Theta s(\vec{n},\pi)\}$, A($\vec{n}$)M($\vec{n}'$) with $\vec{n} \perp \vec{n}'$, A ⊗ T and E = $\{-\mathbf{1}, \mathbf{1}\}$

- ✓ Multi-reference wave-function at the cost of HF ($\propto N^3$)!
- ✓ Simple application of perturbation theory (property calculations)
- ✗ Possibility for unphysical mixtures of configurations
- ✗ Wave-function has wrong symmetry
- ✗ Difficult to describe low-spin states

H. Fukutome, *Int. J. Quantum Chem.* **1981**, *20*, 955–1065.

The ground state energy is fully determined by the one-electron four-current $j^{\mu}(\vec{r})$:

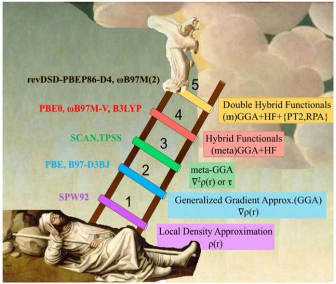
$$j^{\mu}(\vec{r}_1) = N \int \cdots \int \mathrm{d}\vec{r}_2 \cdots \mathrm{d}\vec{r}_N \bar{\Psi}_{4c} \boldsymbol{\gamma}_1^{\mu} \otimes \boldsymbol{\gamma}_2^{0} \otimes \cdots \otimes \boldsymbol{\gamma}_N^{0} \Psi_{4c}\,,$$

Idea: instead of using the complex $3N$ dimensional wave functions minimize energy with respect to $j^{\mu}(\vec{r})$:

$$E[{}^{\mu}(\vec{r})] = \underbrace{T[j^{\mu}(\vec{r})]}_{\text{kinetic energy}} + \underbrace{V_{\mathrm{ext}}[j^{\mu}(\vec{r})]}_{\text{external potential (incl e-N interaction)}} + \underbrace{V_{\mathrm{H}}[j^{\mu}(\vec{r})]}_{\text{Hartree potential (classical Coulomb repulsion)}} + \underbrace{E_{\mathrm{XC}}[j^{\mu}(\vec{r})]}_{\text{exchange correlation functional}}$$

Problem: Exact closed expression for E_{XC} unknown.

- ✓ DFT is formally exact
- ✓ DFT can be formulated consistently with QFT
- ✓ Pure Kohn-Sham DFT is of lower cost than HF ($N(N+1)/2N_{\mathrm{grid}}$)
- ✗ E_{XC} is unknown
- ✗ Semi-empiricial estimates of E_{XC} introduce systematic errors
- ✗ Relativistic calculations rely currently on non-relativistic E_{XC}



P. Hohenberg, W. Kohn, *Phys. Rev. B* **1964**, *136*, 864–871, A. K. Rajagopal, J. Callaway, *Phys. Rev. B* **1973**, *7*, 1912–1919.
J. Martin, G. Santra, *Israel. J. Chem.* **2019**, *60*, DOI 10.1002/ijch.201900114.

A crash course in relativistic molecular structure
Adiabatic approximation/Born–Oppenheimer approximation

Nuclei are assumed to be non-relativistic!

Table 1. Three frequently discussed adiabatic approximations

	I Crude adiabatic approximation	II Born–Oppenheimer adiabatic approximation	III Born–Huang adiabatic approximation
Adiabatic wavefunction	$\Psi_{jt}^{\mathrm{CA}}(r,Q)=\psi_j^0(r,Q_0)\chi_{jt}^{\mathrm{CA}}(Q)$	$\Psi_{jt}^{\mathrm{BO}}(r,Q)=\psi_j(r,Q)\chi_{jt}^{\mathrm{BO}}(Q)$	$\Psi_{jt}^{\mathrm{BH}}(r,Q)=\psi_j(r,Q)\chi_{jt}^{\mathrm{BH}}(Q)$
Electronic equation	$[T_e(r)+U(r,Q_0)-\epsilon_j^0(Q_0)]\times\psi_j^0(r,Q_0)=0$	$[T_e(r)+U(r,Q)-\epsilon_j(Q)]\times\psi_j(r,Q)=0$	$[T_e(r)+U(r,Q)-\epsilon_j(Q)]\times\psi_j(r,Q)=0$
Vibrational equation	$[T_N(Q)+V(Q)+\epsilon_j^0(Q_0)+\langle\psi_j^0(r,Q_0)\vert\Delta U(r,Q)\vert\psi_j^0(r,Q_0)\rangle-E_{jt}^{\mathrm{CA}}]\chi_{jt}^{\mathrm{CA}}(Q)=0$	$[T_N(Q)+V(Q)+\epsilon_j(Q)-E_{jt}^{\mathrm{BO}}]\times\chi_{jt}^{\mathrm{BO}}(Q)=0$	$[T_N(Q)+V(Q)+\epsilon_j(Q)+\langle\psi_j(r,Q)\vert T_N(Q)\vert\psi_j(r,Q)\rangle-E_{jt}^{\mathrm{BH}}]\chi_{jt}^{\mathrm{BH}}(Q)=0$
Adopted approximation	$\langle\psi_j^0(r,Q_0)\vert\Delta U(r,Q)\vert\psi_k^0(r,Q_0)\rangle=0$ for $k\neq j$	$\langle\psi_j(r,Q)\vert T_N(Q)\vert\psi_k(r,Q)\rangle=0$ and $\left\langle\psi_j(r,Q)\middle\vert\frac{\partial}{\partial Q_n}\middle\vert\psi_k(r,Q)\right\rangle=0$	$\langle\psi_j(r,Q)\vert T_N(Q)\vert\psi_k(r,Q)\rangle=0$ for $k\neq j$ and $\left\langle\psi_j(r,Q)\middle\vert\frac{\partial}{\partial Q_n}\middle\vert\psi_k(r,Q)\right\rangle=0$

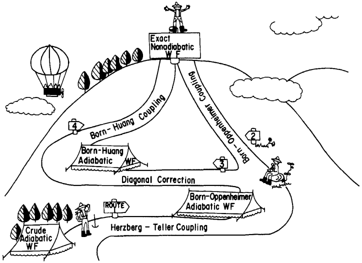


Figure 1. Various routes to approach the exact non-adiabatic wavefunction. As to the three types of adiabatic wavefunctions, see Table 1.

BO is an effective field theory. Perturbation series in the electron-to-proton-mass-ratio:

$$E_{\mathrm{elec}}\propto\sqrt{\frac{m_{\mathrm{e}}}{m_{\mathrm{p}}}}E_{\mathrm{vib}}\propto\frac{m_{\mathrm{e}}}{m_{\mathrm{p}}}E_{\mathrm{rot}}$$

P. R. Bunker, P. Jensen, Molecular Symmetry and Spectroscopy, 2nd ed., NRC Research Press, Ottawa, Ontario, Canada, **2006**, T. Azumi, K. Matsuzaki, *Photochem. Photobiol.* **1977**, *25*, 315–326.

- For small perturbations (new physics effects are definitely small!) $\hat{H}_i$ we can use perturbation theory!
- First order for variational Ψ_j

$$\frac{\partial E}{\partial \lambda_i} = \langle \Psi_j | \hat{H}_i | \Psi_j \rangle$$

- Not true for CC or MPn!
  $\rightarrow$ numeric differentiation (finite field) or perturbation of Lagrangian within response theory!
- For second order:

$$\frac{\partial^2 E}{\partial \lambda_i \delta \lambda_l} = \langle \Psi_j | \hat{H}_{il} | \Psi_j \rangle + \left\langle \frac{\partial \Psi_j}{\partial \lambda_l} \middle| \hat{H}_i \middle| \Psi_j \right\rangle + \mathrm{hc}$$

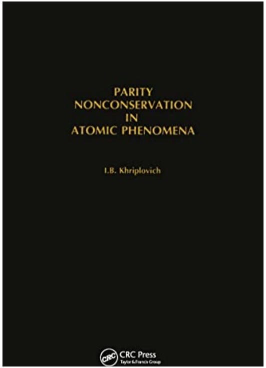
$$\left\langle \frac{\partial \Psi_j}{\partial \lambda_l} \middle| \hat{H}_i \middle| \Psi_j \right\rangle = \sum_{aj} \frac{\langle \Psi_j | \hat{H}_i | \Psi_a \rangle \langle \Psi_a | \hat{H}_l | \Psi_j \rangle}{E_j - E_a}$$

Depends on excited states!

$\Longrightarrow$ HF/DFT level: Linear response theory (random phase approximation, RPA)

P. Norman et al., Principles and Practices of Molecular Properties, John Wiley & Sons, Ltd, **2018**.

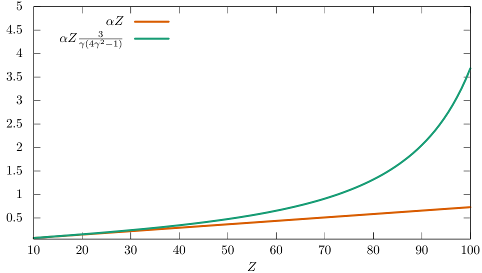
1933 Fermi and Segré: simple effective one-electron approach to describe hyperfine coupling constants within quantum defect theory.
1958 Improvement of the model by Foldy.
1972 Generalization of the model by Fröman and Fröman.
1975 Bouchiat and Bouchiat: extend it to parity violation.



- Simple effective one-electron wave functions at distances $r \ll a_0 Z^{-1/3}$:

$$f_\kappa(r) = \frac{\kappa}{|\kappa| r \sqrt{Z a_0 \nu_\kappa^3}} \left((\kappa + \gamma_\kappa) J_{2\gamma_\kappa}\left(\sqrt{\frac{8Zr}{a_0}}\right) - \sqrt{\frac{2Zr}{a_0}} J_{2\gamma_\kappa - 1}\left(\sqrt{\frac{8Zr}{a_0}}\right)\right),$$

$$g_\kappa(r) = \frac{\kappa Z \alpha}{|\kappa| r \sqrt{Z a_0 \nu_\kappa^3}} J_{2\gamma_\kappa}\left(\sqrt{\frac{8Zr}{a_0}}\right),$$



- Effective quantum numbers ν contain all many-body information ($\mathcal{O}(\nu_\kappa) \sim 1$!)

$\Longrightarrow$ Estimate the expectable order of magnitude of a property!

$\Rightarrow$Fundamental symmetry violating properties are often relativistically enhanced!

E. Fermi, E. Segrè, *Z. Phys.* **1933**, *82*, 729–749, L. L. Foldy, *Phys. Rev.* **1958**, *111*, 1093–1098, N. Fröman, P. O. Fröman, *Phys. Rev. A* **1972**, *6*, 2064–2067, C. Bouchiat, M. A. Bouchiat, *J. Phys. (Paris)* **1975**, *36*, 493–509.

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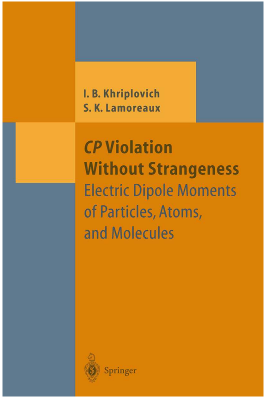

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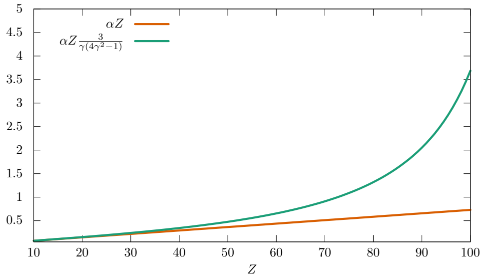

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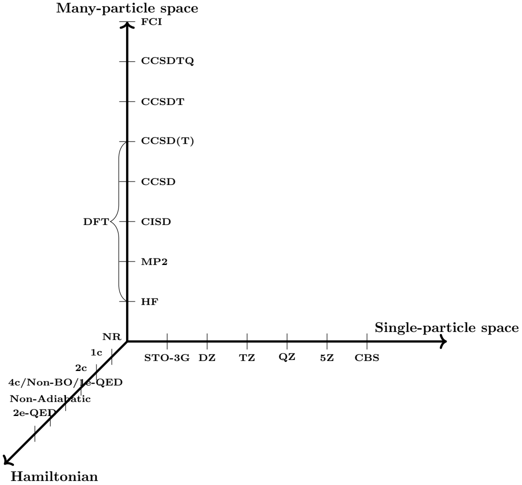
- For identifying molecular probes **DFT** usually sufficient (if **open-shell broken-symmetry HF/DFT**!)
- Broken symmetries appear in the valence: **Two-component** methods are quantitative $< 1\,\%$
- Standard basis sets are not designed for physics beyond the Standard Model properties! $\rightarrow$ **Be very careful!**
- Assisting spectroscopy requires usually accurate predictions with relative errors $< 10\%$
- Extraction of limits on new physics is dependent on the theory uncertainty and requires
  - Highly correlated methods (CC, MRCI, etc.) if the uncertainty is limited by electronic structure
  - HF/DFT is usually OK if the uncertainty is limited by nuclear structure
- Second order properties can be tough!



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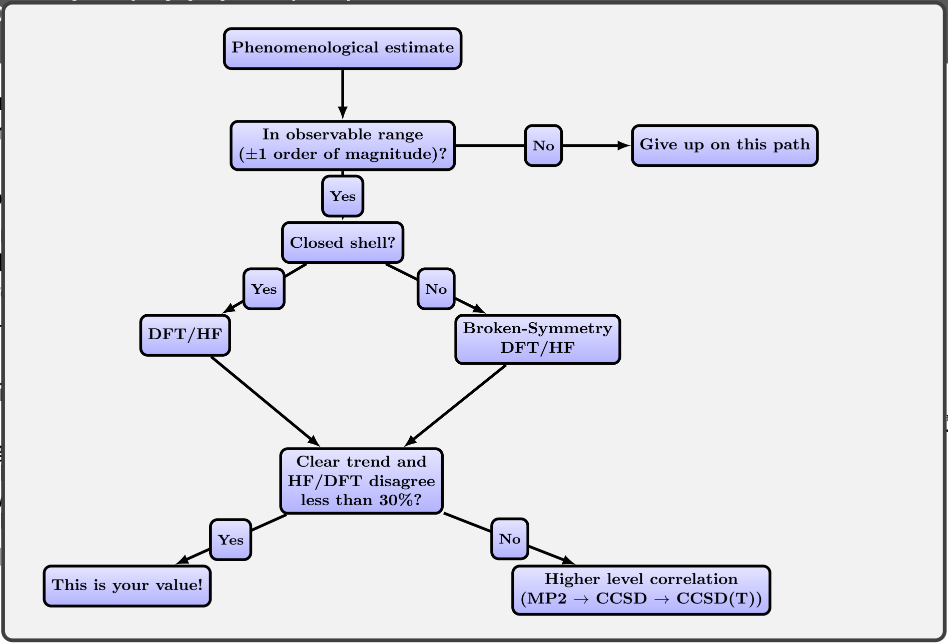

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