Towards variational QED

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Negative energy states in classical mechanics

- Non-relativistic free particle:

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}; \quad \Rightarrow \quad E \in [0, \infty\rangle$$

- Relativistic free particle:

$$E^2 = m^2c^4 + c^2p^2; \quad \Rightarrow \quad E \in \langle -\infty, -mc^2] \cup [+mc^2, \infty\rangle$$

- We can ignore the negative energy states since the energy can only change in a *continuous* manner
- We can connect the non-relativistic and relativistic energy expression by a Taylor-expansion of the former

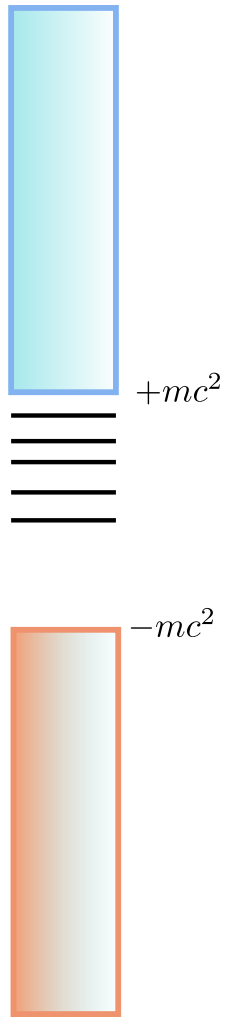
$$E = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}} = \underbrace{mc^2}_{\text{rest mass}} + \underbrace{\frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots}_{\text{kinetic energy}}$$

Negative-energy states in quantum mechanics

- Dirac equation for an electron in a molecular field

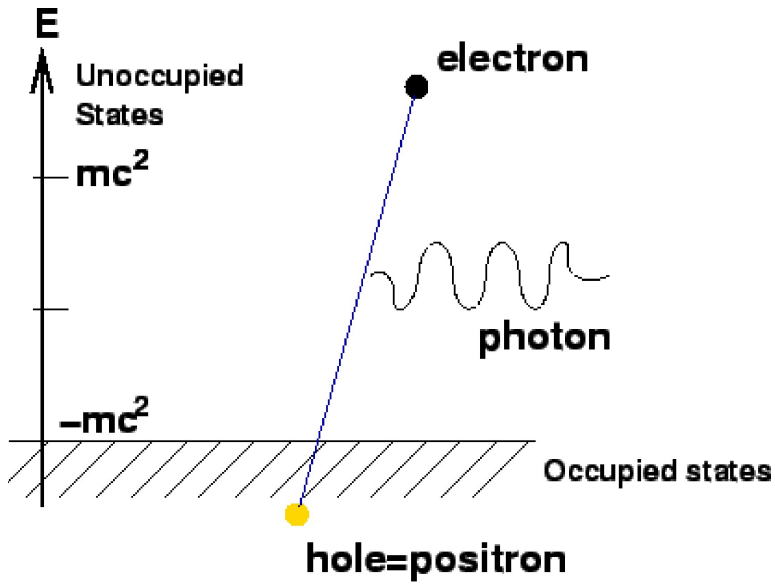
$$\begin{bmatrix} V + mc^2 & c\,(\boldsymbol{\sigma} \cdot \mathbf{p}) \\ c\,(\boldsymbol{\sigma} \cdot \mathbf{p}) & V - mc^2 \end{bmatrix} \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} = \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} E$$

- Negative energy solutions can *not* be ignored, since quantum leaps are allowed
- **Problem:**
  - Matter is not stable !
  - The hydrogen atom would have a lifetime of about a nanosecond...



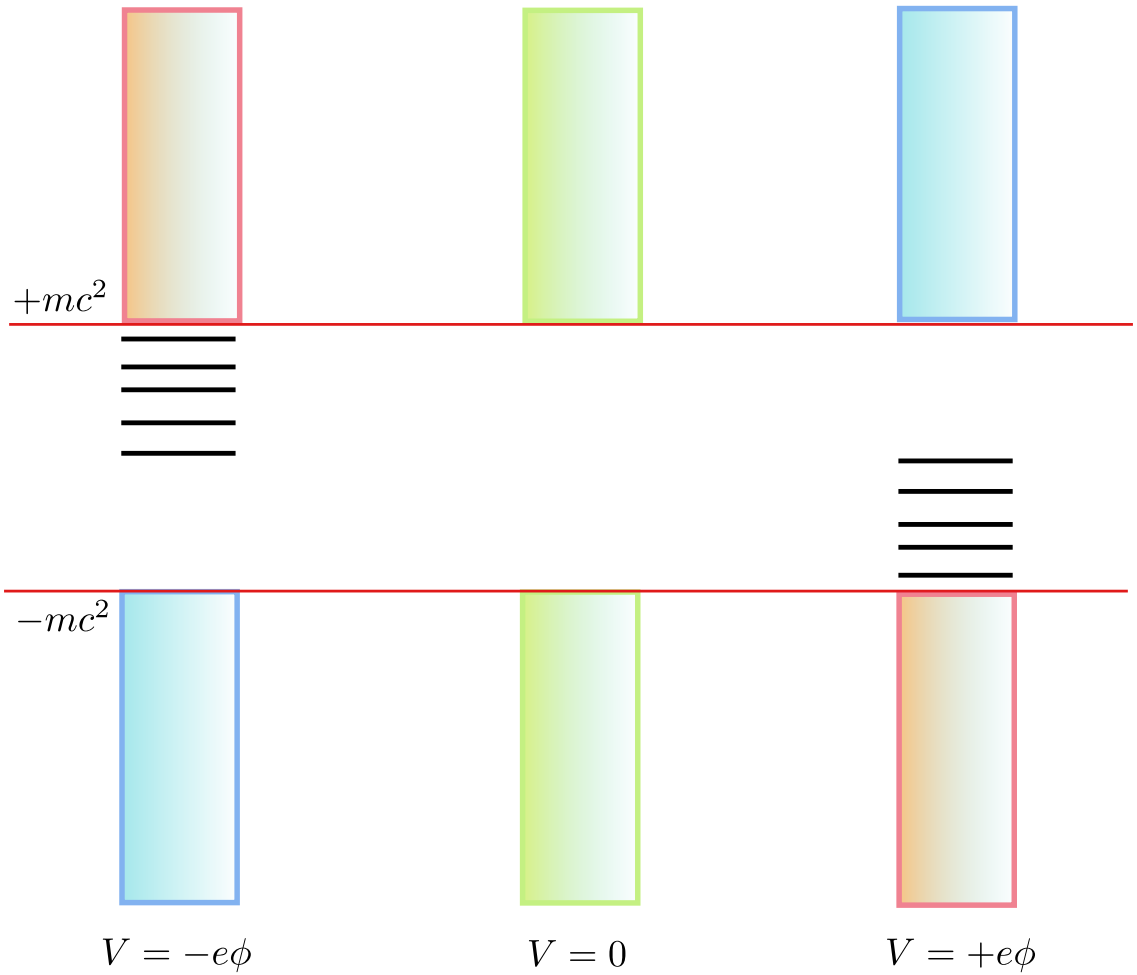
Anti-particles

- **The solution proposed by Dirac**
  - All negative-energy solutions are occupied.
  - The Pauli exclusion principle then hinder electrons descending down the negative-energy branch.
  - The excitation of an electron from the negative-energy band leaves a hole of positive charge, corresponding to the creation of a electron-positron pair.



The theory of Dirac is confirmed in 1932 when the US physicist Carl Anderson discovers the positron.

Charge conjugation symmetry



External fields are introduced through minimal substitution

$$\hat{\mathbf{p}} \to \hat{\boldsymbol{\pi}} = \hat{\mathbf{p}} - q\mathbf{A}; \quad E \to E + q\phi$$

Non-relativistic two-electron atom

E. Hylleraas, Naturwissenschaften 17 (1929) 982

- One-electron problem (point nucleus)

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right]\varphi_Z(\mathbf{r}) = \varepsilon_Z\varphi_Z(\mathbf{r})$$

- Coordinate scaling $r \to Z^{-1}r$:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}\right]\varphi_{Z=1}(\mathbf{r}) = \varepsilon_{Z=1}\varphi_{Z=1}(\mathbf{r}); \quad \varepsilon_Z = Z^2\varepsilon_{Z=1}$$

  - Two-electron problem:

$$\left[\hat{h}_{Z=1}(1) + \hat{h}_{Z=1}(2) + \frac{1}{Z}V_{ee}\right]\Psi(1,2) = E'\Psi(1,2); \quad E = Z^2E'$$

  - The two-electron interaction appears as perturbation with Z^{-1} as corresponding perturbation parameter

Perturbational solution

- Correlation energy:

$$E_c = E^{exact} - E^{HF}$$

  - where E^{exact} will be taken to be full CI.

- Perturbation theory:
  - Both HF and Ci starts from the same zeroth-order function

$$\Phi_0 = \left|\varphi_{1s}^{(0)}\alpha\varphi_{1s}^{(0)}\beta\right|$$

  - ... so that zeroth and first-order energy corrections are identical

$$E_0 = \left\langle 0\left|\hat{H}_0\right|0\right\rangle = 2\varepsilon_{1s} = -Z^2$$

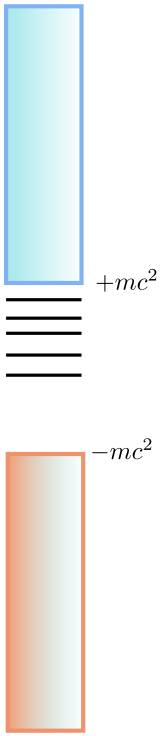
$$E_1 = \left\langle \Phi_0\left|\hat{H}_1\right|\Phi_0\right\rangle = \left\langle \varphi_{1s}^{(0)}\varphi_{1s}^{(0)}|\varphi_{1s}^{(0)}\varphi_{1s}^{(0)}\right\rangle = \frac{5}{8}Z$$

  - Correlation energy:

$$E_c = E_2^{CI} - E_2^{HF} + O\left(Z^{-1}\right) = \sum_{ia}\frac{\langle ij \parallel ab\rangle\langle ab \parallel ij\rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} + O\left(Z^{-1}\right)$$

(the MP2-like expression is evaluated using the orbitals of the one-electron problem)

Relativistic two-electron atoms



- Proceeding as before

$$E_c = \sum_{ia} \frac{\langle ij \parallel ab \rangle \langle ab \parallel ij \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} + O\left(Z^{-1}\right)$$

- **Problem:**

  An infinite number of doubly excited Slater determinants Φ_{ij}^{ab} are degenerate with the reference determinant Φ_0

- The Dirac-Coulomb Hamiltonian has no bound solutions ! [G. E. Brown and D. G. Ravenhall, Proc. Roy. Soc. London A **208** (1951) 552]

- **No-pair approximation:** embedding the DC Hamiltonian by projection operators onto positive energy orbitals [J. Sucher, Phys. Rev. A 22 (1980) 348]

$$H^{DC} \quad \rightarrow \quad \Lambda_+ H^{DC} \Lambda_+$$

- The negative-energy solutions are treated as an orthogonal complement

QED effects in chemistry?

- In the past thirty years it has become clear that relativistic effects are important for the theoretical description of molecules containing heavy atoms
- We seek to investigate the importance of QED effects on molecular electronic structure and properties
- QED effects reduce relativistic effects by about one percent

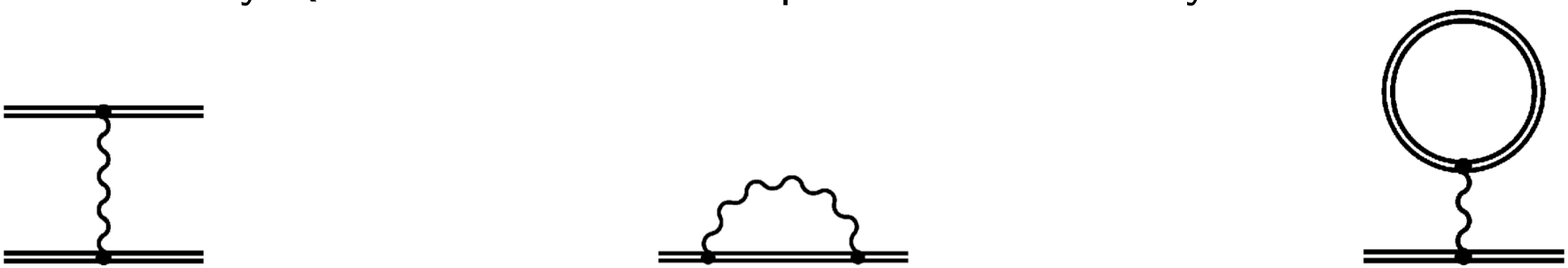
  K. G. Dyall and C. W. Bauschlicher and D. W. Schwenke and P. Pyykkö, "Is the Lamb shift chemically significant?", Chem. Phys. Lett. **348** (2001) 497.
- However, this study was limited to valence properties. QED effects are probably more important for properties that sample the electron density near nuclei, such as NMR parameters. A study by Pyykkö and Zhao indicate that for NMR parameters QED effects could have the same importance as solvent effects

  P. Pyykkö and L.-B. Zhao, "Search for effective local model potentials for simulation of quantum electrodynamic effects in relativistic calculations", J. Phys. B. **36** (2003) 1469

Present-day QED

- QED is a marvel of modern science,
  allowing predictions of accuracy beyond that of experiment
- Yet QED in its present formulation only allows precise calculations on few-electron atomic systems
- Extension to many-electron molecular systems may be possible through effective QEDpotentials

  E.A. Uehling, Phys. Rev. **48** (1935) 55; P. Pyykkö and L.-B. Zhao, J. Phys. B, **36** (2003) 1469; V. M. Shabaev, I. I. Tupitsyn, and V. A. Yerokhin, Phys. Rev. A, **88** (2013) 012513; V.V. Flambaum, J.S.M. Ginges, Phys. Rev. A **72** (2005) 052115
  - ...but such potentials are designed for energy corrections, not properties
- Present-day QED is formulated as perturbation theory



- Here we go for a variational formulation

Short bibliography

- The present work is based on
  T. Saue and L. Visscher: "Four-component electronic structure methods for molecules" in S. Wilson and U. Kaldor (eds.): "Theoretical chemistry and physics of heavy and superheavy elements", Kluwer, Dordrecht 2003
- Related work:
  - P. Chaix and D. Iracane: *From quantum mechanics to mean-field theory: I. The Bogoliubov-Dirac-Fock formalism*, J.Phys.B **22** (1989) 3791
  - P.Chaix and D. Iracane: *From quantum mechanics to mean-field theory: II. Variational stability of the vacuum of quantum electrodynamics in the mean-field approximation*, J.Phys.B **22** (1989) 3815
  - *C. Hainz, M. Lewin & J.P. Solovej. The mean-field approximation in Quantum Electrodynamics. The no-photon case. Comm. Pure Appl. Math.* **60** *(2007) 546*
  - W. Kutzelnigg: *Solved and unsolved problems in relativistic quantum chemistry*, Chem. Phys. **395** (2011) 16
  - W. Liu and I. Lindgren: *Going beyond "no-pair relativistic quantum chemistry"*, J. Chem. Phys. **139** (2013) 014108
  - W. Greiner, B. Müller and J. Rafaelski: *Quantum Electrodynamics of Strong Fields: With an Introduction into Modern Relativistic Quantum Mechanics*, Springer-Verlag 1985

Second quantization

- The electron density can be obtained from the quantity

$$\rho(1) = N \int \Psi^{\dagger}(1, 2, \ldots, N)\, \Psi(1, 2, \ldots N)\, d2 \ldots dN$$

- The electron density integrates to the number of electrons

$$\int \rho(1)\, d1 = N.$$

- We now introduce an **operator**

$$\hat{N} = \int \hat{\psi}^{\dagger}(1)\, \hat{\psi}(1)\, d1$$

- ... in terms of operators $\hat{\psi}^{\dagger}(1)$ and $\hat{\psi}(2)$, creating and annihilating electron density amplitude at position 1, respectively.
- We want the total operator $\hat{N}$ to return the particle number N, when acting on an object representing an N-electron system.

Field operators

- In order to represent electrons (fermions) field operators must obey the following anti-commutation relations

$$\left[\hat{\psi}^\dagger(1),\hat{\psi}^\dagger(2)\right]_+ = \hat{\psi}^\dagger(1)\hat{\psi}^\dagger(2)+\hat{\psi}^\dagger(2)\hat{\psi}^\dagger(1) = 0$$

$$\left[\hat{\psi}(1),\hat{\psi}(2)\right]_+ = \hat{\psi}(1)\hat{\psi}(2)+\hat{\psi}(2)\hat{\psi}(1) = 0$$

$$\left[\hat{\psi}(1),\hat{\psi}^\dagger(2)\right]_+ = \hat{\psi}(1)\hat{\psi}^\dagger(2)+\hat{\psi}^\dagger(2)\hat{\psi}(1) = \delta(1-2)$$

- Bosons obey corresponding commutator relations.

Quantum field theory

- The field operators do not relate to specific electrons; rather, they sample contributions to the **electron quantum field** in space

- Quantum field theory explains why electrons are the same everywhere; they all belong to the same field !

Expansion of field operators

- Suppose that we have some orthonormal orbital basis $\{\varphi_p(1)\}_{p=1}^{M}$

$$\int \varphi_p^\dagger(1)\varphi_q(1)d1 = \langle\varphi_p|\varphi_q\rangle = S_{pq} = \delta_{pq}$$

- We now expand the field operators in this basis

$$\hat{\psi}(1) = \sum_q \varphi_q(1)\hat{a}_q; \quad \hat{\psi}^\dagger(1) = \sum_q \varphi_q^\dagger(1)\hat{a}_q^\dagger$$

- We find the expansion coefficients $\hat{a}_p$ and $\hat{a}_p^\dagger$ by

$$\hat{a}_p = \int \varphi_p^\dagger(1)\hat{\psi}(1)d1; \quad \hat{a}_p^\dagger = \int \hat{\psi}^\dagger(1)\varphi_p(1)d1$$

  - $\hat{a}_p$ is denoted an annihilation operator
  - $\hat{a}_p^\dagger$ is denoted a creation operator and is the conjugate of $\hat{a}_p$

Annihilation and creation operators

- The algebra of the annihilation and creation operators follows from the algebra of the field operators. We have

$$\left[\hat{\psi}(1), \hat{\psi}^\dagger(2)\right]_+ = \delta(1-2)$$

- .. from which we deduce

$$\left[\hat{a}_p, \hat{a}_q^\dagger\right]_+ = \left[\int \varphi_p^\dagger(1)\hat{\psi}(1)d1, \int \hat{\psi}^\dagger(2)\varphi_q(2)d2\right]_+$$

- Further manipulation gives

$$\begin{aligned}
\left[\hat{a}_p, \hat{a}_q^\dagger\right]_+ &= \int\int \varphi_p^\dagger(1)\varphi_q(2)\left[\hat{\psi}(1), \hat{\psi}^\dagger(2)\right]_+ d1d2 \\
&= \int\int \varphi_p^\dagger(1)\varphi_q(2)\delta(1-2)d1d2 \\
&= \int \varphi_p^\dagger(1)\varphi_q(1)d1 = \delta_{pq}
\end{aligned}$$

Algebra of annihilation and creation operators

- We just found that (using an orthonormal basis)

$$\left[\hat{\psi}(1), \hat{\psi}^\dagger(2)\right]_+ = \delta(1-2) \quad \Rightarrow \quad \left[\hat{a}_p, \hat{a}_q^\dagger\right]_+ = \delta_{pq}$$

- In a similar manner we find that

$$\left[\hat{\psi}^\dagger(1), \hat{\psi}^\dagger(2)\right]_+ = 0 \quad \Rightarrow \quad \left[\hat{a}_p^\dagger, \hat{a}_q^\dagger\right]_+ = 0$$

$$\left[\hat{\psi}(1), \hat{\psi}(2)\right]_+ = 0 \quad \Rightarrow \quad \left[\hat{a}_p, \hat{a}_q\right]_+ = 0$$

Occupation-number vectors

- Let us consider a simple example:
  We have 4 orbitals $\{\varphi_1, \varphi_2, \varphi_3, \varphi_4\}$ (M=4).
- With two electrons (N=2) we can build $\begin{pmatrix} 4 \\ 2 \end{pmatrix} = 6$ determinants.

  One example is

$$\Phi(1,2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \varphi_1(1) & \varphi_3(1) \\ \varphi_1(2) & \varphi_3(2) \end{vmatrix}$$

- or, in short-hand notation

$$\Phi(1,2) = |\varphi_1 \varphi_3|$$

- We can map this into an **occupation-number vector**

$$\Phi_k(1,2) = |\varphi_1 \varphi_3| \quad \rightarrow \quad |k\rangle = |k_1, k_2, k_3, k_4\rangle = |1,0,1,0\rangle$$

- ... where *occupation numbers* k_p are either 0 or 1,
  since electrons are fermions.

Occupation-number vectors

Vacuum state and annihilation

- Another example is

$$\Phi_m(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \varphi_4(1) \\ \varphi_1(2) & \varphi_2(2) & \varphi_4(2) \\ \varphi_1(3) & \varphi_2(3) & \varphi_4(3) \end{vmatrix} = |\varphi_1\varphi_2\varphi_4| \quad \rightarrow \quad |\Phi_m\rangle = |1,1,0,1\rangle$$

- A special occupation-number vector is the **vacuum state**

$$|vac\rangle = |0,0,0,0\rangle$$

- Annihilation operators reduce occupation numbers by one and therefore all give zero when acting on $|vac\rangle$

$$\hat{a}_p\,|vac\rangle = 0; \quad \forall \hat{a}_p$$

- This even serves as a definition of the vacuum state.

Operators

- The number operator counts electrons

$$\hat{N} = \int \hat{\psi}^\dagger(1)\hat{\psi}(1)d1 = \sum_{pq}\left\{\int \varphi_p^\dagger(1)\varphi_q(1)d1\right\}\hat{a}_p^\dagger\hat{a}_q = \sum_p \hat{a}_p^\dagger\hat{a}_p$$

- There is also an operator for counting electron pairs

$$\hat{N}_{pair} = \frac{1}{2}\int \hat{\psi}^\dagger(1)\hat{\psi}^\dagger(2)\hat{\psi}(2)\hat{\psi}(1)\mathrm{d1d2} = \frac{1}{2}\sum_{pq}\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_q\hat{a}_p = \frac{1}{2}\hat{N}\left(\hat{N}-1\right)$$

- The second-quantized Hamiltonian

$$\hat{H} = \int \hat{\psi}^\dagger(1)\hat{h}(1)\hat{\psi}(1)\mathrm{d1} + \frac{1}{2}\int \hat{\psi}^\dagger(1)\hat{\psi}^\dagger(2)\hat{g}(1,2)\hat{\psi}(2)\hat{\psi}(1)\mathrm{d1d2} + V_{NN}$$

  (notice the order of electron coordinates in the two-electron operator)

- This gives a formula for finding the second-quantized form of any one- and two-electron operator.

Notation/Summary

- Einstein summation convention employed throughout
- Field operators: can be expanded in different one-particle bases defining in turn different sets of creation and annihilation operators

$$\hat{\psi}(1) = \varphi_p(1)\, a_p = \widetilde{\varphi}_p(1)\, \widetilde{a}_p$$

- Second-quantized Hamiltonian

$$\begin{aligned}
\hat{H} &= \int \hat{\psi}^\dagger(1) \underbrace{\hat{h}(1)}_{\text{Dirac}} \hat{\psi}(1) d\tau_1 \\
&+ \frac{1}{2} \int\int \hat{\psi}^\dagger(1)\hat{\psi}^\dagger(2) \underbrace{\hat{g}(1,2)}_{\text{Coulomb}} \hat{\psi}(2)\hat{\Psi}\hat{\psi}(1) d1 d2 \\
&= h_{pq} a_p^\dagger a_q + \frac{1}{4}\mathcal{L}_{pq,rs} a_p^\dagger a_r^\dagger a_s a_q
\end{aligned}$$

- Anti-symmetrized two-electron integrals: $\mathcal{L}_{pq,rs} = (pq \mid rs) - (ps \mid rq)$
- Orbital classes

$$\underbrace{a, b, c, d}_{\text{virtual}}, \ldots \underbrace{i, j, k, l}_{\text{occupied}}, \ldots \underbrace{p, q, r, s}_{\text{general}}, \ldots$$

Hartree–Fock theory in second quantization

- Starting from a selected orbital set $\{\varphi_p\}$,
  Slater determinants (Hilbert space) map into occupation-number vectors (Fock space)

$$|\Phi\rangle = a_1^\dagger a_2^\dagger \dots a_N^\dagger |vac\rangle$$

  which are eigenfunctions of the number operator $\hat{N} = a_p^\dagger a_p$
- The vacuum state is the occupation-number vector giving zero when acted upon by all annihilaton operators

$$a_p |vac\rangle = 0; \quad \forall a_p$$

- Hartree-Fock variational ansatz: exponential parameterization

$$\left|\widetilde{\Phi}\right\rangle = \exp\left[-\widehat{\kappa}\right] |\Phi\rangle ; \quad \widehat{\kappa} = \kappa_{pq} a_p^\dagger a_q; \quad \kappa_{pq} = -\kappa_{qp}^*$$

Hartree–Fock theory in second quantization

- The Hartree-Fock variational ansatz can be re-written as

$$\begin{aligned}\left|\widetilde{\Phi}\right\rangle &= \exp\left[-\widehat{\kappa}\right]|\Phi\rangle = \widehat{U}a_1^\dagger a_2^\dagger \ldots a_N^\dagger |vac\rangle \\ &= \widehat{U}a_1^\dagger \widehat{U}^\dagger \widehat{U}a_2^\dagger \widehat{U}^\dagger \widehat{U} \ldots \widehat{U}^\dagger \widehat{U}a_N^\dagger \widehat{U}^\dagger \widehat{U}|vac\rangle \\ &= \widetilde{a}_1^\dagger \widetilde{a}_2^\dagger \ldots \widetilde{a}_N^\dagger |vac\rangle\end{aligned}$$

- Transformed creation operators

$$\widetilde{a}_p^\dagger = \exp\left[-\widehat{\kappa}\right] a_p^\dagger \exp\left[\widehat{\kappa}\right] = a_q^\dagger U_{qp}; \quad U = \exp\left[-\kappa\right]$$

- **Important:** To derive the above we have used

$$\exp\left[-\widehat{\kappa}\right]|vac\rangle = \left(1 - \kappa_{pq}a_p^\dagger a_q + \ldots\right)|vac\rangle = |vac\rangle$$

Hartree-Fock theory in second quantization

Transformed creation operator

- To connect to orbital rotations we recall the formula

$$a_p^\dagger = \int \hat{\psi}^\dagger(\mathbf{r})\varphi_p(\mathbf{r})\mathrm{d}^3\mathbf{r}$$

- ...from which we obtain

$$\tilde{a}_r^\dagger = \sum_p a_p^\dagger \left\{\exp\left[-\kappa\right]\right\}_{pr} = \sum_p \int \hat{\psi}^\dagger(\mathbf{r})\varphi_p(\mathbf{r}) \left\{\exp\left[-\kappa\right]\right\}_{pr} \mathrm{d}^3\mathbf{r} = \int \hat{\psi}^\dagger(\mathbf{r})\tilde{\varphi}_r(\mathbf{r})\mathrm{d}^3\mathbf{r}$$

- which provides the connection

$$\left|\widetilde{\Phi}\right\rangle = \exp\left(-\hat{\kappa}\right)\left|\Phi\right\rangle \quad \Rightarrow \quad \tilde{\varphi}_r = \sum_p \varphi_p(\mathbf{r}) \left\{\exp\left[-\kappa\right]\right\}_{pr}$$

Relativistic Hartree-Fock theory

- Hartree–Fock energy:

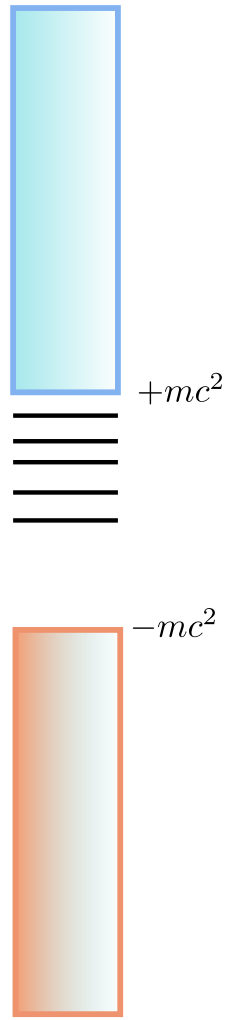
$$E^{\mathrm{HF}}\left[\{\varphi_i\}\right] = h_{ii} + \frac{1}{2}\mathcal{L}_{ii,jj}$$

- The orbitals are found from solving an effective one-electron equation

$$\hat{F}\left[\{\varphi_i\}\right]\varphi_p = \varepsilon_p \varphi_p$$

  which has solutions of both positive and negative energy

- Minmax principle (Talman 1957)
  - $\left\{\kappa_{ia}^{++}\right\}$: minimize
  - $\left\{\kappa_{ia}^{+-}\right\}$: maximize
- ... corresponds to the implicit use of projection operator
- It is updated in every SCF iteration and kept frozen at the correlated level (**no-pair approximation**)



Towards QED

- Conventional 4-component relativistic calculations are based on the no-pair approximation: $\Lambda_+ H^{DC} \Lambda_+$ where the negative-energy orbitals are treated as an orthogonal complement.
- In QED the negative-energy orbitals take on physical reality to describe the polarizable vacuum
- I will consider QED in the semiclassical limit, that is without quantization of electromagnetic fields.
- Particle-hole formalism

$$\hat{\psi} = \varphi_p a_p \quad \rightarrow \quad \hat{\psi} = \varphi_p^+ b_p + \varphi_p^- d_p^\dagger$$

  - *electron* annihilation operators b_p associated with the positive-energy electronic orbitals φ_p^+
  - *positron* creation operators $d_p^\dagger$ describing the creation of positrons whose orbitals are obtained by charge conjugating the associated negative-energy electronic orbitals φ_p^-

The QED Hamiltonian

$$
\begin{aligned}
\hat{H} \quad = \quad & h_{pq}^{++}\, b_p^\dagger b_q + h_{pq}^{+-}\, b_p^\dagger d_q^\dagger + h_{pq}^{-+}\, d_p b_q + h_{pq}^{--}\, d_p d_q^\dagger \\
+ \quad & \frac{1}{4}\mathcal{L}_{pqrs}^{++++}\, b_p^\dagger b_r^\dagger b_s b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{+-++}\, b_p^\dagger b_r^\dagger b_s d_q^\dagger + \frac{1}{4}\mathcal{L}_{pqrs}^{+++-}\, b_p^\dagger b_r^\dagger d_s^\dagger b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{+-+-}\, b_p^\dagger b_r^\dagger d_s^\dagger d_q^\dagger \\
+ \quad & \frac{1}{4}\mathcal{L}_{pqrs}^{++-+}\, b_p^\dagger d_r b_s b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{+--+}\, b_p^\dagger d_r b_s d_q^\dagger + \frac{1}{4}\mathcal{L}_{pqrs}^{++--}\, b_p^\dagger d_r d_s^\dagger b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{+---}\, b_p^\dagger d_r d_s^\dagger d_q^\dagger \\
+ \quad & \frac{1}{4}\mathcal{L}_{pqrs}^{-+++}\, d_p b_r^\dagger b_s b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{--++}\, d_p b_r^\dagger b_s d_q^\dagger + \frac{1}{4}\mathcal{L}_{pqrs}^{-++-}\, d_p b_r^\dagger d_s^\dagger b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{--+-}\, d_p b_r^\dagger d_s^\dagger d_q^\dagger \\
+ \quad & \frac{1}{4}\mathcal{L}_{pqrs}^{-+-+}\, d_p d_r b_s b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{---+}\, d_p d_r b_s d_q^\dagger + \frac{1}{4}\mathcal{L}_{pqrs}^{-+--}\, d_p d_r d_s^\dagger b_q + \frac{1}{4}\mathcal{L}_{pqrs}^{----}\, d_p d_r d_s^\dagger d_q^\dagger
\end{aligned}
$$

- The QED Hamiltonian couples occupation-number vectors with different particle number, but conserves charge.

Hartree-Fock theory in semiclassical QED

- Reference occupation-number vector (bound electronic states):

$$|\Phi\rangle = b_1^\dagger b_2^\dagger \dots b_n^\dagger |vac\rangle$$

- QED vacuum state

$$(b_p |vac\rangle = 0, \quad \forall b_p) \quad \text{and} \quad (d_p |vac\rangle = 0, \quad \forall d_p)$$

- Variational Hartree-Fock *ansatz:*

$$\left|\widetilde{\Phi}\right\rangle = \exp\left[-\widehat{\kappa}\right] |\Phi\rangle$$

- Orbital rotation operator:

$$\widehat{\kappa} = \underbrace{\kappa_{pq}^{++} b_p^\dagger b_q}_{\widehat{\kappa}^{++}} + \underbrace{\kappa_{pq}^{+-} b_p^\dagger d_q^\dagger}_{\widehat{\kappa}^{+-}} + \underbrace{\kappa_{pq}^{-+} d_p b_q}_{\widehat{\kappa}^{-+}} + \underbrace{\kappa_{pq}^{--} d_p d_q^\dagger}_{\widehat{\kappa}^{--}}$$

Number and charge operators

- Number operators

$$\hat{N}^e = b_p^\dagger b_p \quad \text{and} \quad \hat{N}^p = d_p^\dagger d_p$$

  - The $\hat{\kappa}$ operator commutes with neither number operator

$$\left[\hat{\kappa}, \hat{N}^e\right] = \left[\hat{\kappa}, \hat{N}^p\right] = \hat{\kappa}^{-+} - \hat{\kappa}^{+-}$$

- Charge operator

$$\hat{Q}_N = e\left(\hat{N}^p - \hat{N}^e\right)$$

  - The orbital rotation operator of QED conserves charge but *not* the particle number:

$$\left[\hat{\kappa}, \widehat{Q}_N\right] = 0$$

Vacuum polarization

- Using the unitarity of the orbital rotation operator we may now rewrite the HF ansatz as

$$\left|\widetilde{\Phi}\right\rangle = \exp\left[-\widehat{\kappa}\right]|\Phi\rangle = \widetilde{b}_1^\dagger \widetilde{b}_2^\dagger \ldots \widetilde{b}_n^\dagger \,|\widetilde{vac}\rangle$$

- Transformed creation operators

$$\widetilde{b}_p^\dagger = \exp\left[-\widehat{\kappa}\right] b_p^\dagger \exp\left[\widehat{\kappa}\right] = b_q^\dagger U_{qp}; \quad U = \exp\left[-\kappa\right]$$

- The dressed vacuum

$$\begin{aligned} |\widetilde{vac}\rangle &= \exp\left[-\widehat{\kappa}\right]|vac\rangle = \\ &= \left\{1 - \kappa_{pq}^{++} b_p^\dagger b_q - \kappa_{pq}^{+-} b_p^\dagger d_q^\dagger - \kappa_{pq}^{-+} d_p b_q - \kappa_{pq}^{--} d_p d_q^\dagger + O(\kappa^2)\right\}|vac\rangle \\ &\neq |vac\rangle \end{aligned}$$

Vacuum expectation values

- The vacuum expectation value of the charge operator is zero

$$\left\langle vac \left| \hat{Q}_N \right| vac \right\rangle = e \left\langle vac \left| \left(\hat{N}^p - \hat{N}^e \right) \right| vac \right\rangle = e \left\langle vac \left| \left(d_p^\dagger d_p - b_p^\dagger b_p \right) \right| vac \right\rangle$$

- However, the vacuum expectation value of the Hamiltonian is infinite

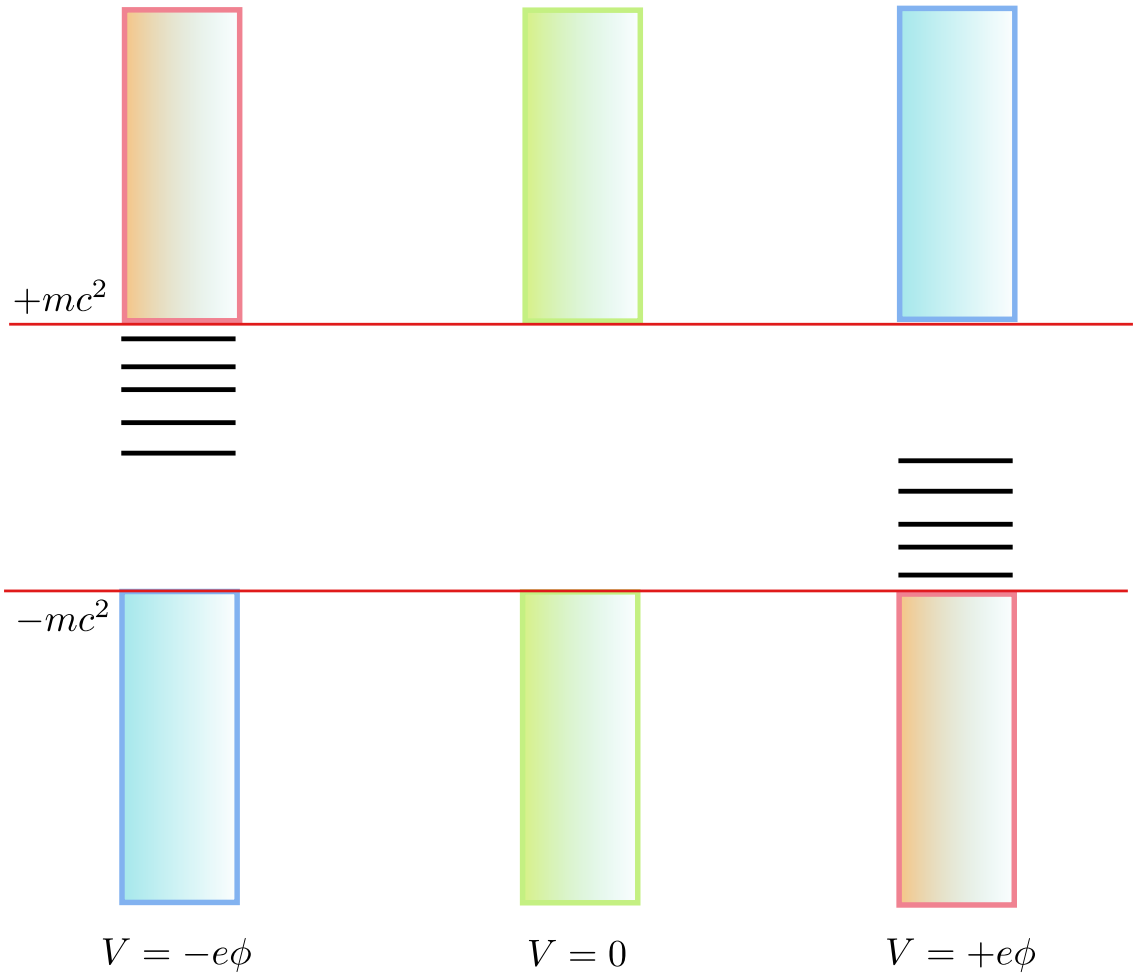
$$\begin{aligned} \left\langle vac \left| \hat{H} \right| vac \right\rangle &= \left\langle vac \left| \ldots h_{pq}^{--} d_p d_q^\dagger \ldots + \frac{1}{4} \mathcal{L}_{pqrs}^{----} d_p d_r d_s^\dagger d_q^\dagger \ldots \right| vac \right\rangle \\ &= h_{ii}^{--} + \frac{1}{2} \mathcal{L}_{iijj}^{----} \end{aligned}$$

- The infinite negative energy is avoided by writing the Hamiltonian on *normal ordered* form

$$\hat{H}_N = \hat{H} - \left\langle vac \left| \hat{H} \right| vac \right\rangle .$$

  - The question is:
    - What vacuum should be used ?

Choice of reference vacuum



A reasonable choice is the free-particle vacuum built from orbitals $\left\{\varphi^{-}_{[i]}\right\}$.

Re-ordering of field vectors

- The normal-ordered QED Hamiltonian

$$\begin{aligned}\hat{H}_N &= \int \left\{\Psi^\dagger(1)\hat{h}(1)\Psi(1)\right\} d1 \\ &+ \frac{1}{2}\int\int \left\{\Psi^\dagger(1)\Psi^\dagger(2)\hat{g}(1,2)\Psi(2)\Psi(1)\right\} d1d2\end{aligned}$$

- From Wick's theorem we obtain:

$$\begin{aligned}\left\{\hat{\psi}(1)\hat{\psi}(2)\right\} &= \varphi_{[p]}(1)\varphi_{[q]}(2)\left\{\hat{a}_p\hat{a}_q\right\} \\ &= \varphi_{[p]}(1)\varphi_{[q]}(2)\left(\hat{a}_p\hat{a}_q - \left\{\overbrace{\hat{a}_p^\dagger}\hat{a}_q\right\}\right) \\ &= \hat{\psi}(1)\hat{\psi}(2) - \varphi_{[i]}^{-;\dagger}(1)\varphi_{[i]}^{-}(2)\end{aligned}$$

Re-ordering of field vectors

- With a bit more work we find

$$\begin{aligned}
\left\{\hat{\psi}^\dagger(1)\hat{\psi}^\dagger(2)\hat{\psi}(2)\hat{\psi}(1)\right\} &= \hat{\psi}^\dagger(1)\hat{\psi}^\dagger(2)\hat{\psi}(2)\hat{\psi}(1) \\
&+ \varphi^{-;\dagger}_{[i]}(1)\hat{\psi}^\dagger(2)\varphi^{-}_{[i]}(2)\hat{\psi}(1) + \hat{\psi}^\dagger(1)\varphi^{-;\dagger}_{[i]}(2)\hat{\psi}(2)\varphi^{-}_{[i]}(1) \\
&- \varphi^{-;\dagger}_{[i]}(1)\hat{\psi}^\dagger(2)\hat{\psi}(2)\varphi^{-}_{[i]}(1) - \hat{\psi}^\dagger(1)\varphi^{-;\dagger}_{[i]}(2)\varphi^{-}_{[i]}(2)\hat{\psi}(1) \\
&- \varphi^{-;\dagger}_{[i]}(1)\varphi^{-;\dagger}_{[j]}(2)\varphi^{-}_{[i]}(2)\varphi^{-}_{[j]}(1) \\
&+ \varphi^{-;\dagger}_{[i]}(1)\varphi^{-;\dagger}_{[j]}(2)\varphi^{-}_{[j]}(2)\varphi^{-}_{[i]}(1)
\end{aligned}$$

- The normal -ordered Hamiltonian accordingly reads:

$$\begin{aligned}
\hat{H}_N &= \hat{H} - \left\langle vac_0 \middle| \hat{H} \middle| vac_0 \right\rangle \\
&= F_{pq}\left[\left\{\varphi^{-}_{[i]}\right\}\right] a^\dagger_p a_q + \frac{1}{4}\mathcal{L}_{pq,rs} a^\dagger_p a^\dagger_r s_s a_q \\
&- \left(h^{--}_{[ii]} + \frac{1}{2}\mathcal{L}^{----}_{[ii,jj]} \right)
\end{aligned}$$

Hartree–Fock energy

- In atomic orbital (AO) basis the conventional HF-energy reads:

$$\varphi_p = \chi_\mu c_{\mu p} \quad \Rightarrow E^{HF} = D_{\mu\nu} h_{\nu\mu} + \frac{1}{2} D_{\mu\nu} \mathcal{L}_{\nu\mu\lambda\kappa} D_{\kappa\lambda}$$

  - AO-density matrix $D_{\lambda\kappa} = \sum_i^{(+)} c_{\lambda i} c^*_{\kappa i}$

- Introducing vacuum polarisation

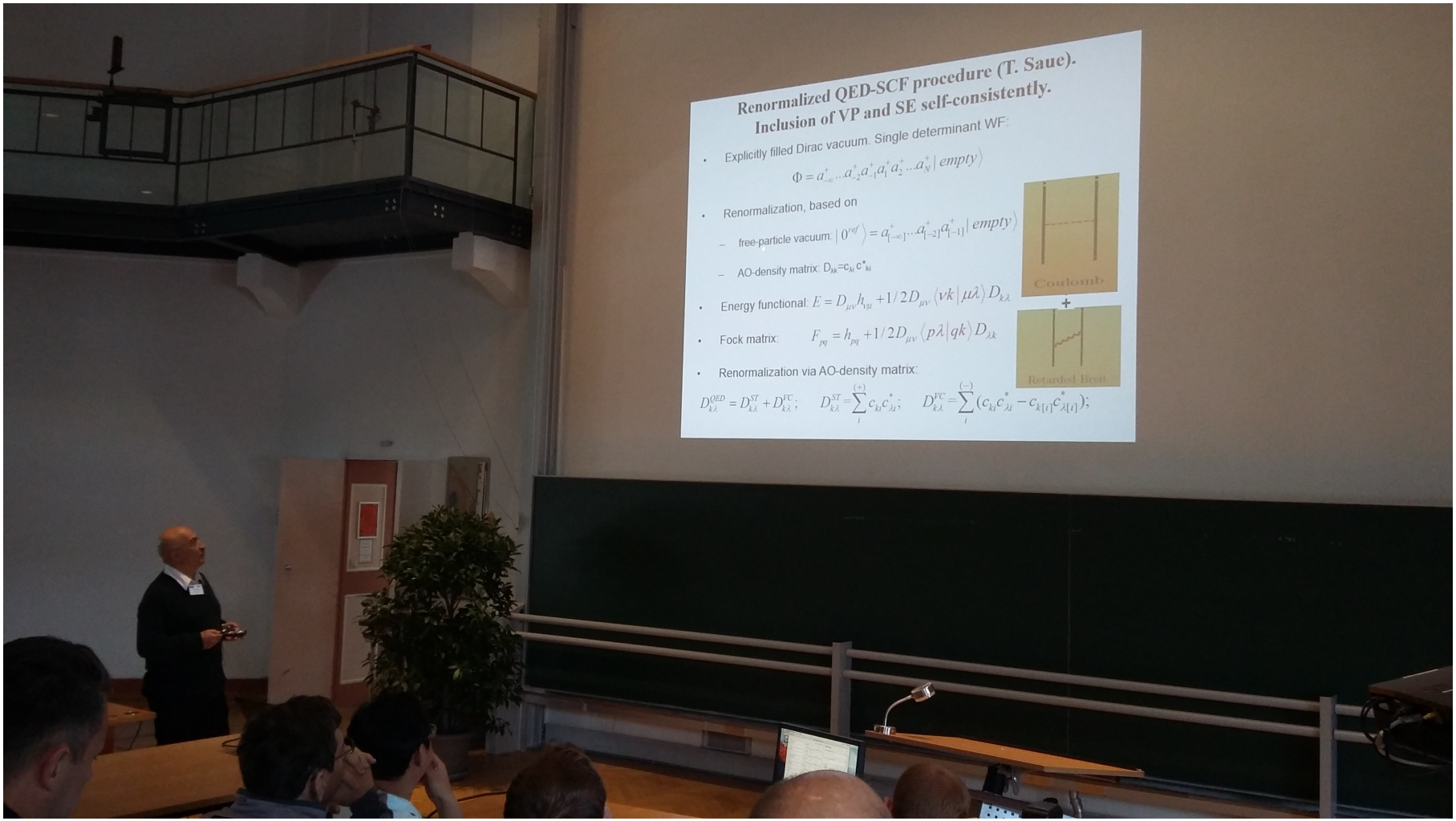
$$D^{HF}_{\lambda\kappa} \rightarrow D^{\mathrm{QED}}_{\kappa\lambda} = D^{HF}_{\kappa\lambda} + D^{\mathrm{VP}}_{\kappa\lambda}; \quad D^{\mathrm{VP}}_{\kappa\lambda} = \sum_i^{(-)} \left(c_{\kappa i} c^*_{\lambda i} - c_{\kappa[i]} c^*_{\lambda[i]} \right)$$

- ...and the associated vacuum polarisation density

$$\rho^{VP}(\mathbf{r}) = -e n^{VP}(\mathbf{r}) = -e D^{\mathrm{VP}}_{\kappa\lambda} \chi_\lambda(\mathbf{r}) \chi_\kappa(\mathbf{r})$$

Good news

REHE2017, Marburg, Sep 3 2017, talk by Ephraim Eliav



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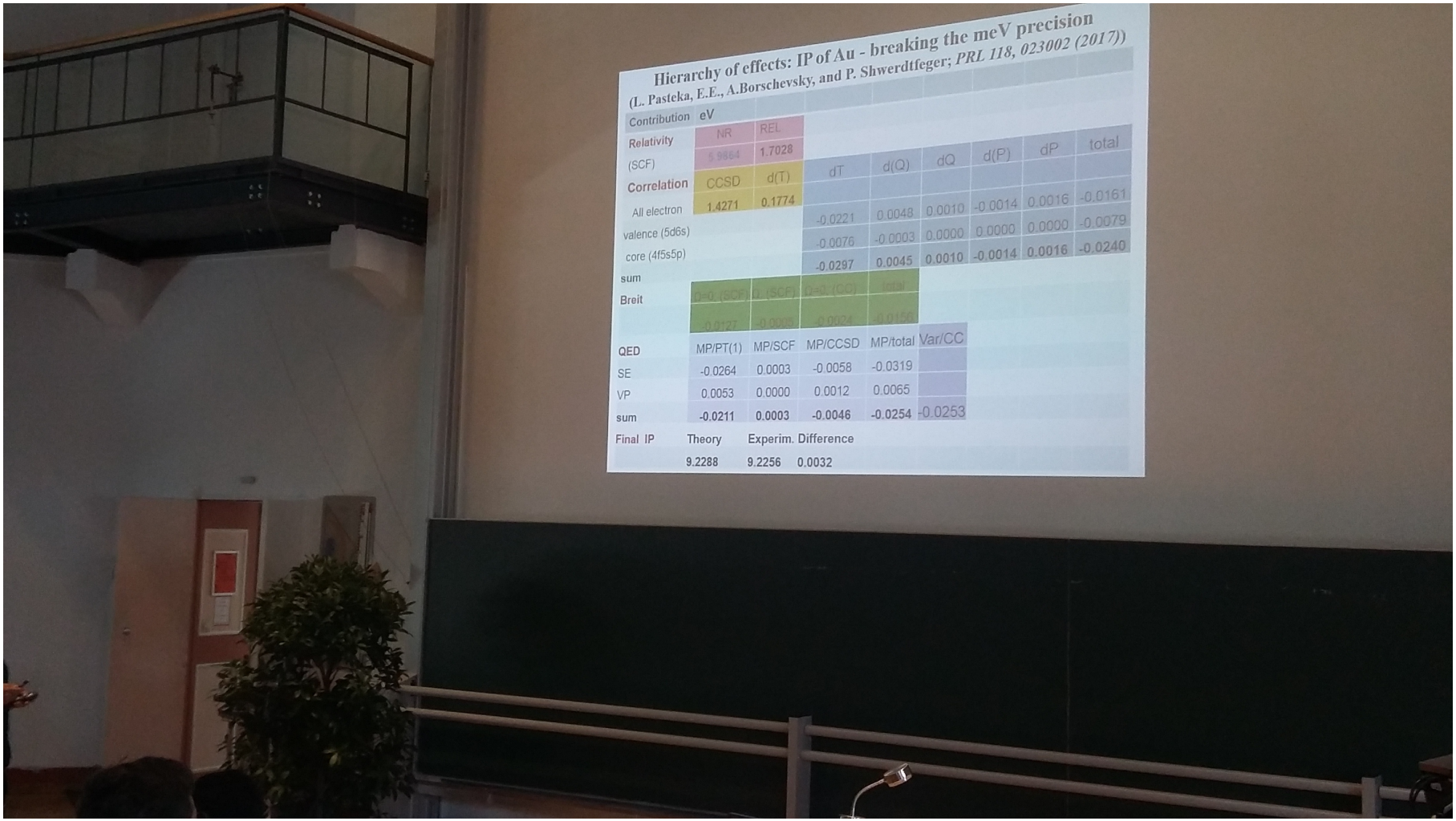

Good news

REHE2017, Marburg, Sep 3 2017, talk by Ephraim Eliav

QED	MP/PT(1)	MP/SCF	MP/CCSD	MP/total	Var/CC
SE	-0.0264	0.0003	-0.0058	-0.0319	
VP	0.0053	0.0000	0.0012	0.0065	
sum	-0.0211	0.0003	-0.0046	-0.0254	-0.0253

Final IP	Theory	Experim.	Difference
	9.2288	9.2256	0.0032

Conclusion and perspectives

- I have presented a theory that allows the introduction of vacuum polarization (and self-energy) into a variational framework.
- However, numerical studies indicate that there are regularization problems to tackle.
  - This should preferably be done in coordinate space, contrary to momentum space of conventional QED
- This is where the hard work starts.
- Recent Fock-space coupled cluster calculations by Ephraim Eliav are very promising and will be explored.
- The present scheme may take QED outside the perturbative regime
  - ... and may be extended to other forces than electromagnetic ones.