# Relativistic many-body perturbation calculations for transition amplitudes in atoms with two valence electrons

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# (I) Foundation of the relativistic atomic many-body theory

- **Dirac-Coulomb Hamiltonian**

$$H = T + V$$

**where**

$$T = \sum_i h_i(\vec{r}_i)$$

$$h(\vec{r}) = c\vec{\alpha} \cdot \vec{p} + \beta mc^2 - \frac{Z}{r}$$

$$V = \sum_{i<j} \frac{1}{r_{ij}}$$

- **Continuum dissolution**

**The Dirac-Coulomb Hamiltonian has no normalizable eigenfunctions.**

**Ref. G. E. Brown and D. G. Ravenhall, Proc. R. Soc. A208, 552 (1951).**

# QED Hamiltonian

- **For Dirac particles interacting via Coulomb interaction**

$$H_{QED}\left|\Phi\right\rangle = E\left|\Phi\right\rangle$$

**where** $$H_{QED} = H_D + H_C$$

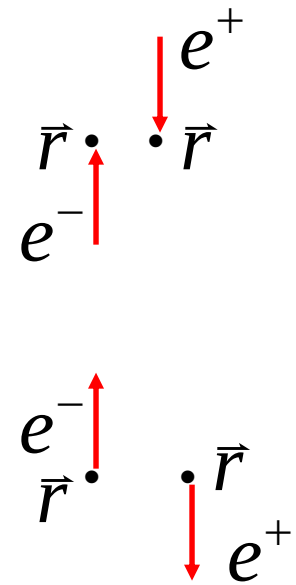
$$H_D = \hat{N}\int d\vec{r}\,\psi^+(\vec{r})h(\vec{r})\psi(\vec{r})$$

$$H_C = \frac{1}{2}\hat{N}\int d\vec{r}\int d\vec{r}'\psi^+(\vec{r})\psi^+(\vec{r}')V_C(\vec{r},\vec{r}')\psi(\vec{r}')\psi(\vec{r})$$

$$V_C(\vec{r},\vec{r}') = \frac{1}{\left|\vec{r}-\vec{r}'\right|}$$

# Furry picture

- **Dirac field operators**




$$\psi(\vec{r}) = \sum_{E_n>0} a_n \phi_n(\vec{r}) + \sum_{E_m<0} b_m^+ \phi_m(\vec{r})$$

$$\psi^+(\vec{r}) = \sum_{E_n>0} a_n^+ \phi_n^+(\vec{r}) + \sum_{E_m<0} b_m \phi_m^+(\vec{r})$$

**where** $h(\vec{r})\phi_i(\vec{r}) = E_i \phi_i(\vec{r})$

$a_n(a_n^+)$: **destruction (creation) operator for electrons** $\vec{r}$

$b_m(b_m^+)$: **destruction (creation) operator for positions**

# No-pair approximation

- **An eigenstate of** $H_{QED}$ **with charge** $-|e|N$

$$|\Phi\rangle = |\Phi_0\rangle + |\Phi_1\rangle + \cdots$$

$|\Phi_0\rangle$: **N electrons**

$|\Phi_1\rangle$: **N electrons plus a pair**

**N-electron state**

$$|\Phi_0\rangle = \int d\vec{r}_1 \cdots d\vec{r}_N \psi^+(\vec{r}_1) \cdots \psi^+(\vec{r}_N) \Psi_0(\vec{r}_1, \cdots, \vec{r}_N) |0\rangle$$

**No-pair approximation:** $|\Phi\rangle \cong |\Phi_0\rangle$

# No-pair Hamiltonian

- **Fock space**

$$H_{QED}\left|\Phi_0\right\rangle = E\left|\Phi_0\right\rangle$$

- **Configuration space**

$$H_{CS}\Psi_0(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N) = E\Psi_0(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)$$

**No-pair Hamiltonian:**

$$H_{CS} = \sum_{i=1}^{N} h_i(\vec{r}_i) + \sum_{i<j}^{N} \Lambda_+(\vec{r}_i)\Lambda_+(\vec{r}_j)V_C(\vec{r}_i,\vec{r}_j)\Lambda_+(\vec{r}_i)\Lambda_+(\vec{r}_j)$$

**Positive-energy projection operator**

$$\Lambda_+(\vec{r}) = \sum_{E_n>0} \varphi_n^+(\vec{r})\phi_n(\vec{r})$$

# (II)Relativistic Many-Body Perturbation Theory

**The Schrödinger equation** $H|\Psi\rangle = E|\Psi\rangle$

**No-pair Hamiltonian** $H = T + V$

$$T = \sum_i [c\alpha_i \cdot p_i + \beta_i mc^2 - \frac{Z}{r_i}]$$

$$V = \sum_{i<j} \Lambda_+ \frac{1}{r_{ij}} \Lambda_+$$

$\Lambda_+$ :**positive-energy projection operator**

**Partition of the Hamiltonian** $H = H_0 + V_I$

**Model Hamiltonian:** $H_0 = \sum_i h(i)$

$$h = c\vec{\alpha} \cdot \vec{p} + \beta mc^2 - \frac{Z}{r} + U(r)$$

**Perturbation:** $V_I = \sum_{i<j} \Lambda_+ \frac{1}{r_{ij}} \Lambda_+ - \sum_i \Lambda_+ U(r_i) \Lambda_+$

$U(r)$: **Model potential (Hartree-Fock potential)**

# Perturbation expansion in powers of $V_I$

$$E = E^{(0)} + E^{(1)} + \cdots$$

$$|\Psi\rangle = |\Psi^{(0)}\rangle + |\Psi^{(1)}\rangle + \cdots$$

## (I) Zeroth order

$$(H_0 - E^{(0)})|\Psi^{(0)}\rangle = 0$$

## (II) First order

$$(H_0 - E^{(0)})|\Psi^{(1)}\rangle = (E^{(1)} - V_I)|\Psi^{(0)}\rangle$$

# Perturbation expansions in powers of $V_I$

**Atomic energy:**

$$E_I = E_I^{(0)} + E_I^{(1)} + \cdots$$

$$E_F = E_F^{(0)} + E_F^{(1)} + \cdots$$

**Photon Energy:**

$$\omega = \omega^{(0)} + \delta\omega^{(1)} + \cdots$$

$$\omega^{(0)} = E_F^{(0)} - E_I^{(0)}$$

$$\delta\omega^{(1)} = E_F^{(1)} - E_I^{(1)}$$

**Transition operator:**

$$T(\omega) = -c\vec{\alpha} \cdot \vec{A}(\omega)$$

$$T(\omega) = T^{(0)}(\omega) + T^{(1)}(\omega) + \cdots$$

$$T^{(0)}(\omega) = T(\omega^{(0)})$$

$$T^{(1)}(\omega) = \delta\omega^{(1)} \frac{dT(\omega^{(0)})}{d\omega}$$

# Transition Amplitudes

## (1) First order:

$$\left\langle F \middle\| T(\omega) \middle\| I \right\rangle^{(1)} = \left\langle \Psi_F^{(0)} \middle\| T^{(0)}(\omega) \middle\| \Psi_I^{(0)} \right\rangle$$

$$= \left\langle \Psi_F^{(0)} \middle\| T(\omega^{(0)}) \middle\| \Psi_I^{(0)} \right\rangle$$

## (2) Second order:

$$\left\langle F \middle\| T(\omega) \middle\| I \right\rangle^{(2)} = \left\langle \Psi_F^{(1)} \middle\| T(\omega^{(0)}) \middle\| \Psi_I^{(0)} \right\rangle + \left\langle \Psi_F^{(0)} \middle\| T(\omega^{(0)}) \middle\| \Psi_I^{(1)} \right\rangle$$

$$+ \delta\omega^{(1)} \left\langle \Psi_F^{(0)} \middle\| \frac{dT(\omega^{(0)})}{d\omega} \middle\| \Psi_I^{(0)} \right\rangle$$

# Relativistic MBPT calculations

## Step 1: Configuration interaction calculations

**The multiconfiguration zeroth order wave functions account for the *main valence-valence* correlations.**

## Step 2: Perturbation calculations

**The *remaining valence-valence*、 *core-valence* and *core-core* correlations are treated by perturbations.**

# Zeroth order wave function

$$\left|\Psi^{(0)}\right\rangle = \sum_{vw} C_{vw} \left|\Phi_{vw}^{(0)}\right\rangle$$

$\left|\Phi_{vw}^{(0)}\right\rangle$ : **Configuration wave functions**

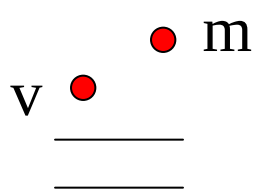
## Be-like ions in the ground state:

$$\left|\Psi^{(0)}\right\rangle = C_1 \left|2s_{1/2}^2\right\rangle + C_2 \left|2p_{1/2}^2\right\rangle + C_3 \left|2p_{3/2}^2\right\rangle$$

# First-order wave function

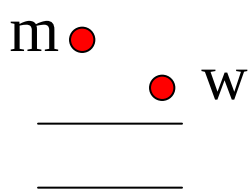
$$\left|\Phi_{vw}^{(1)}\right\rangle = \underbrace{\left|D_{1vw}\right\rangle + \left|D_{2vw}\right\rangle + \left|D_{3vw}\right\rangle}_{\text{valence-valence}} + \underbrace{\left|T_{1vw}\right\rangle + \left|T_{2vw}\right\rangle + \left|T_{3vw}\right\rangle}_{\text{core-valence}} + \underbrace{\left|Q_{vw}\right\rangle}_{\text{core-core}}$$

$$\left|D_{1vw}\right\rangle : \quad a_m^+ a_v^+ \left|0\right\rangle$$



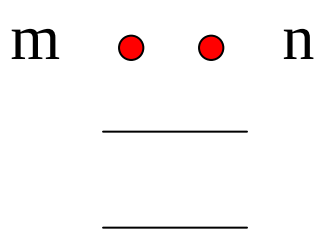

**1v excitation**

$$\left|D_{2vw}\right\rangle : \quad a_m^+ a_w^+ \left|0\right\rangle$$



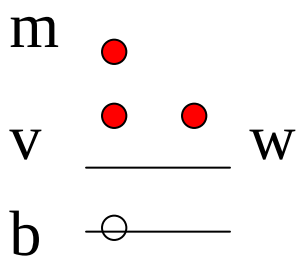

**1v excitation**

$$\left|D_{3vw}\right\rangle : \quad a_m^+ a_n^+ \left|0\right\rangle$$



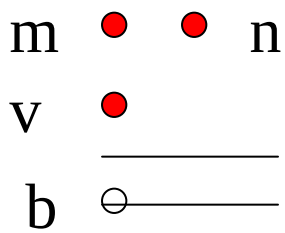

**2v excitation**

$$\left|T_{1vw}\right\rangle : \quad a_m^+ a_b a_v^+ a_w^+ \left|0\right\rangle$$



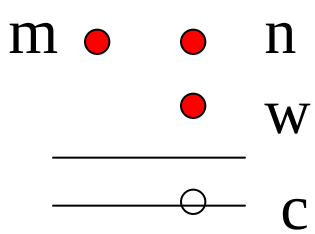

1c excitation

$$\left|T_{2vw}\right\rangle : \quad a_m^+ a_n^+ a_b a_v^+ \left|0\right\rangle$$



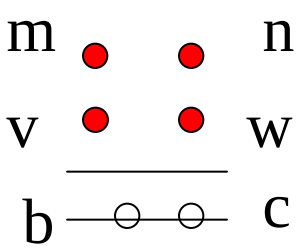

1v-1c excitation

$$\left|T_{3vw}\right\rangle : \quad a_m^+ a_n^+ a_c a_w^+ \left|0\right\rangle$$




1v-1c excitation

$$\left|Q_{vw}\right\rangle : a_m^+ a_n^+ a_c a_b a_v^+ a_w^+ \left|0\right\rangle$$




2c excitation

If $U = V_{HF}$, then $\left|D_{1vw}\right\rangle = \left|D_{2vw}\right\rangle = \left|T_{1vw}\right\rangle = 0$

# First-order Transition Amplitudes

$$\left\langle J'M' \middle\| T \middle\| JM \right\rangle^{(1)} = [J]^{1/2}[J']^{1/2} \sum_{\substack{vw \\ v'w'}} \eta_{v'w'} \eta_{vw} C_{v'w'} C_{vw}$$

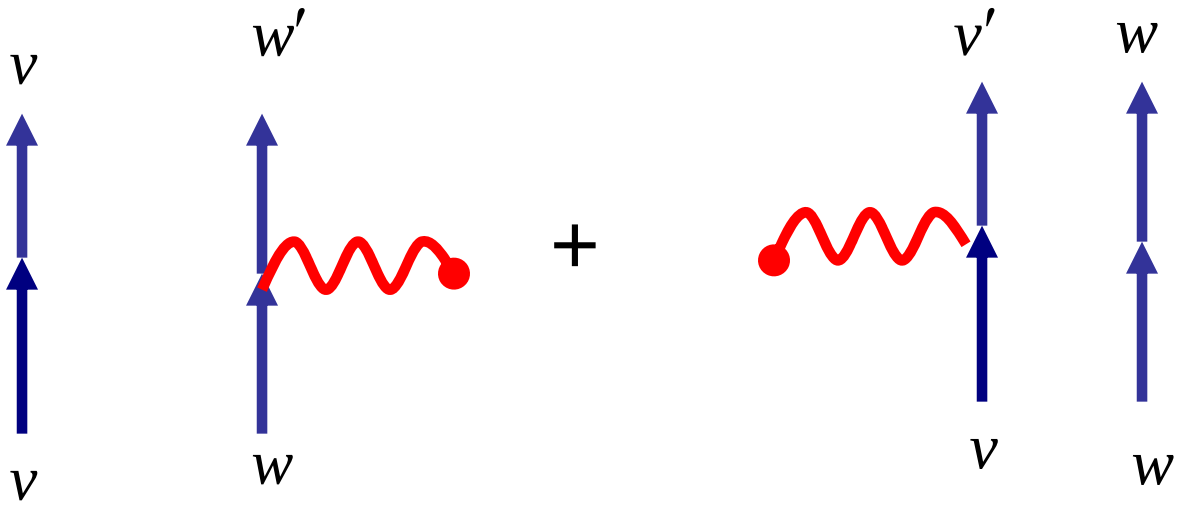
$$\times \left[ (-1)^{J'+j_v+j_w+1} \begin{Bmatrix} J' & J & 1 \\ j_w & j_{w'} & j_v \end{Bmatrix} \left\langle w' \middle\| t \middle\| w \right\rangle \delta_{vv'} \right.$$

$$+ (-1)^{J+j_{v'}+j_{w'}+1} \begin{Bmatrix} J' & J & 1 \\ j_v & j_{v'} & j_w \end{Bmatrix} \left\langle v' \middle\| t \middle\| v \right\rangle \delta_{ww'}$$

$$\left. + (v' \leftrightarrow w') \right]$$

**Ref: H.-S. Chou, Phys. Rev. A62, 42507 (2000)**

# First-order Diagram (4)




$+ \quad (v' \leftrightarrow w')$

# Second-order Transition Amplitudes

$$\left\langle J'M' \middle\| T \middle\| JM \right\rangle^{(2)} = [J]^{1/2}[J']^{1/2} \sum_{\substack{vw \\ v'w'}} \eta_{v'w'} \eta_{vw} C_{v'w'} C_{vw}$$

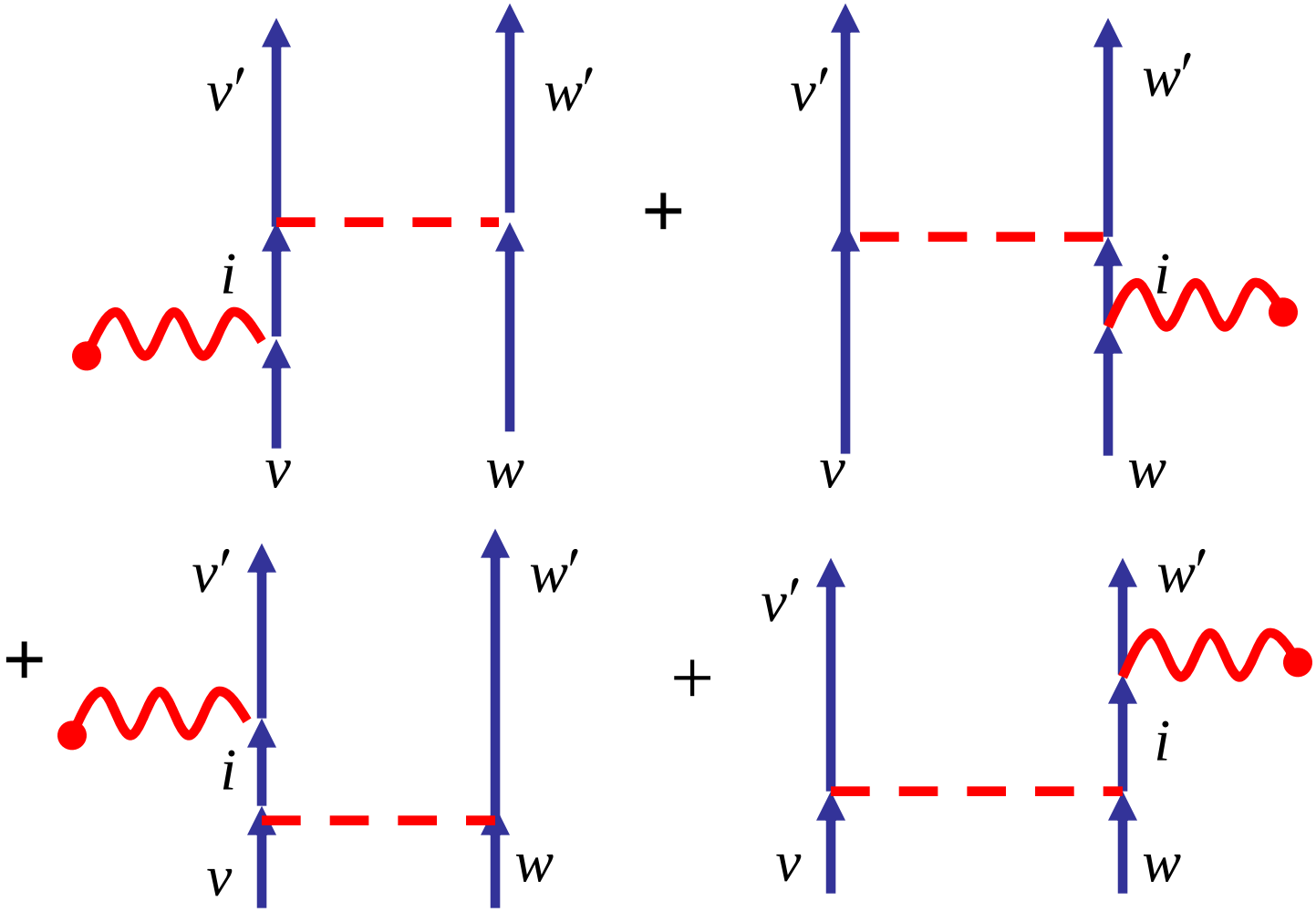
$$\times [\omega^{(0)} \left( Z^{(HF)} + Z^{(val)} + Z^{(RPA)} \right)$$

$$+ \delta\omega^{(1)} \left\langle \Psi^{(0)}_{J'M'} \middle\| dT(\omega^{(0)}) / d\omega \middle\| \Psi^{(0)}_{JM} \right\rangle ]$$

If $U = V_{HF}$ , then $Z^{(HF)} = 0$ .

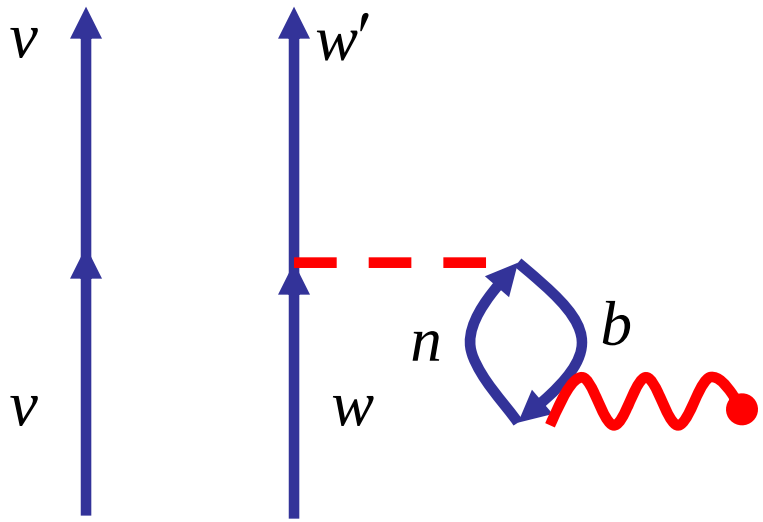
**Ref: H.-S. Chou, Phys. Rev. A62, 42507 (2000)**

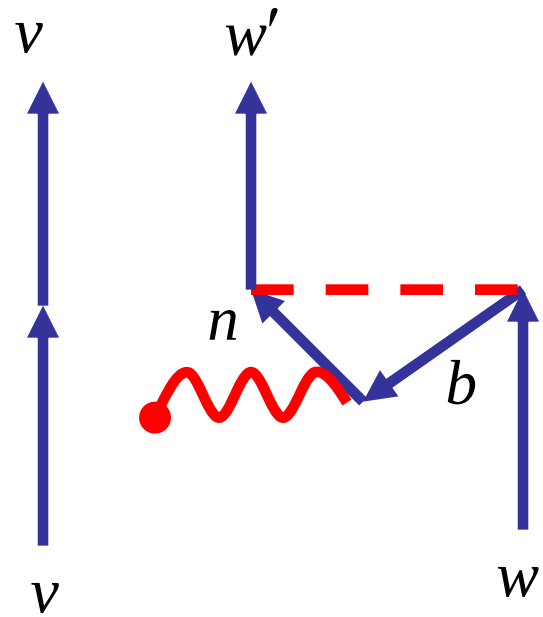
# Second-order Valence-Valence Diagrams (8)




$+ \qquad (v' \leftrightarrow w')$

# Second-order RPA Diagrams (16)



# (III) Results for the Be-like and the Zn-like ions

- **All (9) allowed E1 transitions in the n=2 complex of the Be-like ions.**

  **Ref: H.-S. Chou, Phys. Rev. A62, 42507 (2000)**

- **All (16) allowed E1 transitions among the first fourteen levels in the Zn-like ions.**

  **Ref: H.-C. Chi and H.-S. Chou, Phys. Rev. A82, 032518 (2010)**

# Transition amplitude for the resonance transition in the Be-like ion $S^{12+}$

## (I) Relativistic MBPT

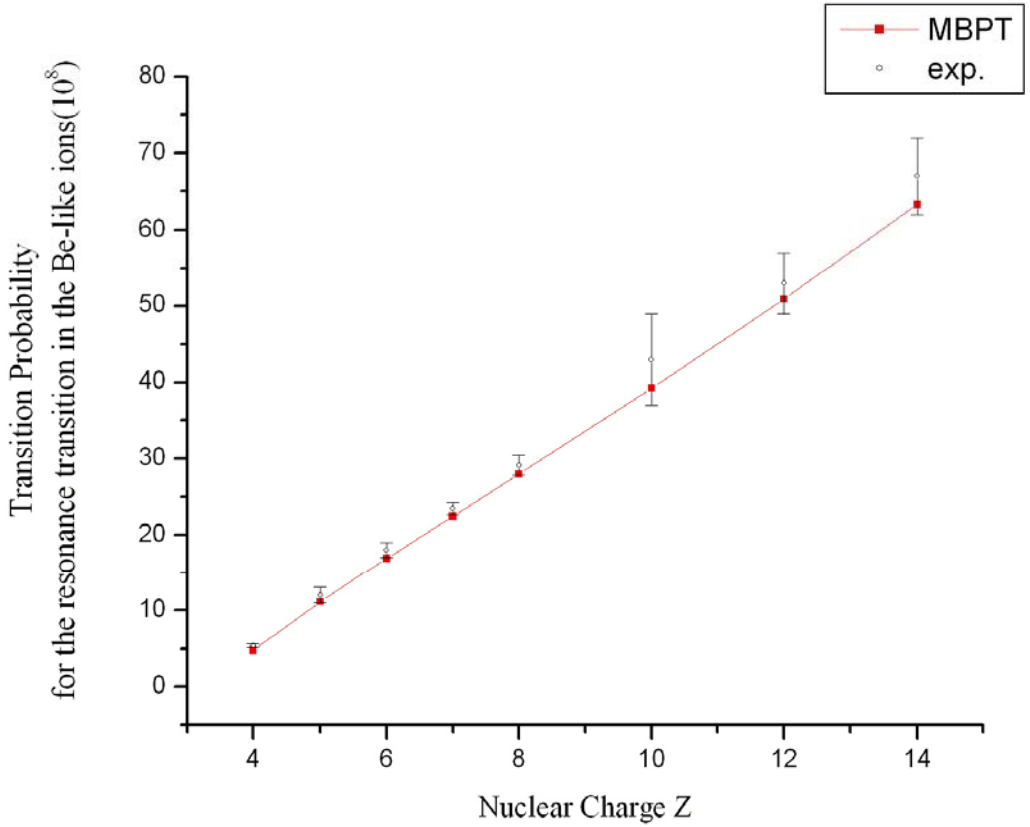
| | length | velocity |
|---|---|---|
| $1^{st}$-order | $1.0005\times10^{-3}$ | $1.6145\times10^{-3}$ |
| $2^{nd}$-order | $9.6348\times10^{-4}$ | $3.4548\times10^{-4}$ |
| total | $1.9640\times10^{-3}$ | $1.9600\times10^{-3}$ |

**Transition amplitudes in different gauges are in excellent agreement !**

## (II) Experiment $(1.9\pm0.1)\times10^{-3}$

**Transition amplitudes from the relativistic MBPT calculations are in excellent agreement with experiment.**

# Transition probability for the resonance transition in the Be-like ions




**The transition probabilities from the 2nd order relativistic MBPT calculations agree well with experiment except for the neutral Be atom. The discrepancy is due to the 3rd order correlations.**

# Transition amplitude for the resonance transition in the Zn-like ion $As^{+3}$

## (I) Relativistic MBPT

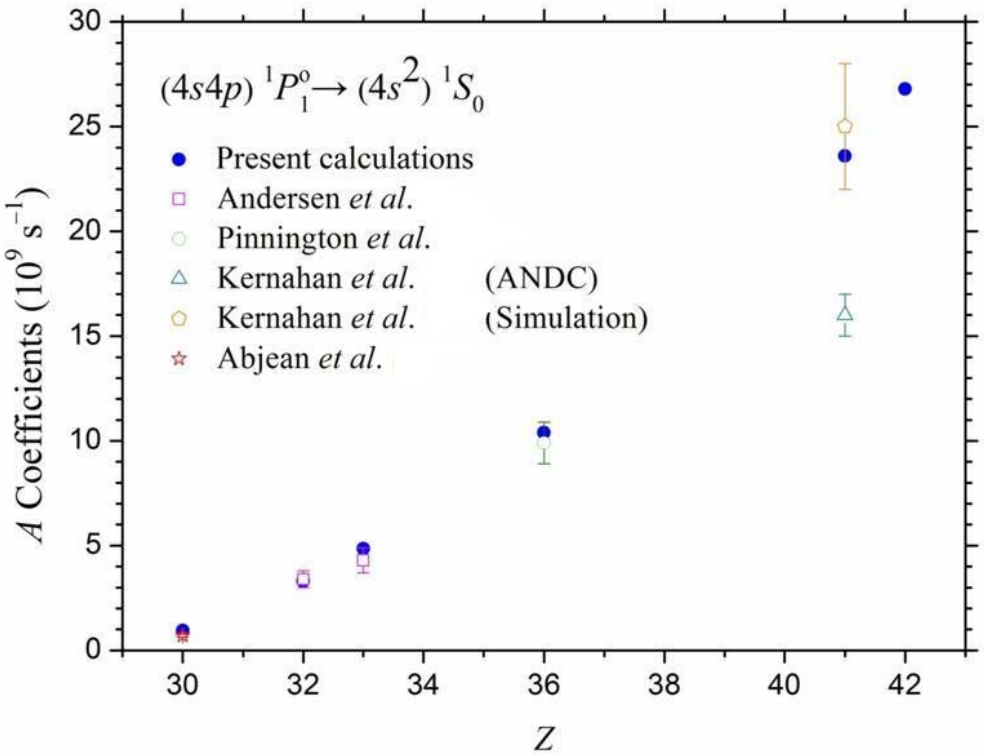
| | length | velocity |
|---|---|---|
| $1^{st}$-order | $-2.451\times10^{-3}$ | $-3.010\times10^{-3}$ |
| $2^{nd}$-order | $-3.592\times10^{-4}$ | $2.137\times10^{-4}$ |
| total | $-2.810\times10^{-3}$ | $-2.796\times10^{-3}$ |

**Transition amplitudes in different gauges are in excellent agreement !**

## (II) Experiment $-(2.7\pm0.2)\times10^{-3}$

**Transition amplitudes from the relativistic MBPT calculations are in excellent agreement with experiment.**

# A coefficients for the resonance transition in the Zn-like ions




**The A coefficients from the 2nd order relativistic MBPT calculations agree well with experiment except for the neutral Zn atom. The discrepancy is due to the 3rd order correlations.**

# Gauge properties of the RMBPT

- **The gauge dependence of the total transition amplitude from the N-th order RMBPT calculation is (N-1)-th power in $V_I$ .**
- **The RMBPT calculation is gauge invariant order by order for calculations starting from local model potential and including the contributions from the negative-energy states.**

**Ref: H.-C. Chi and H.-S. Chou, Phys. Rev. A82, 032518 (2010)**

# Conclusions

- **The transition amplitudes from the second-order relativistic MBPT calculations agree well in different gauges.**
- **The transition amplitudes from the second-order relativistic MBPT calculations are in excellent agreement with experiment for all ions except for the neutral atoms.**

# Future Works

- **We will derive the third-order relativistic MBPT formulas to remove the discrepancies between theory and experiment for neutral atoms.**
- **We will apply the relativistic MBPT to study the photoionization processes.**

Thank you for your attention.