Introduction to Relativistic Quantum Chemistry

Exercises

The exercise classes have as their purpose the consolidation of the lecture material. Therefore, as a general exercise the participants should verify or work through any of the information in the lecture materials which is unclear to them. The exercises given below are in part an attempt to provide concrete examples which will illustrate or clarify the lecture material, and in part are extensions of the material. The student should take these as a sample of exercises, not a complete list.

1. Derive the Lorentz transformation for the x direction.
2. Derive the velocity transformation from $u = dx/dt$.
3. Verify that the Lorentz transformation is symmetric, i.e. invariant to interchange of primed and unprimed variables and the sign of v.
4. Verify that the sum of two velocities ($< c$) cannot exceed c.
5. Derive a Lorentz transformation for the electromagnetic field tensor with the velocity in the x direction. (Consider separate transformations on the 4-vectors A and ∂.)

6. Where is $v > c/\sqrt{2}$ for a particle in a Coulomb potential?
7. Show that the general solution of the Klein-Gordon equation is time-dependent. Under what boundary/initial conditions is the density time-independent?
8. Verify the transition from the Dirac equation to the Klein-Gordon equation.
9. Show that the limits $r \to 0$ and $c \to \infty$ gives a non-zero term in the Dirac equation for a Coulomb potential.

10. Verify that the Dirac equation is Lorentz invariant.
11. Show that the current density $\mathrm{j} = \Psi^\dagger \alpha^\mu \Psi$ is Lorentz invariant
12. Show that $\Psi^\dagger \bar{\Psi} = 0$.

13. For what Z do the large and small components for a $1s$ electron become equal in magnitude?

14. For what Z is the relativistic correction to the energy equal to the nonrelativistic energy for a $1s$ electron?

15. Verify the Baker-Campbell-Hausdorff expansion

$$e^{-\hat{\kappa}}\hat{H}e^{\hat{\kappa}} = \hat{H} + \left[\hat{H}, \hat{\kappa}\right] + \frac{1}{2!}\left[\left[\hat{H}, \hat{\kappa}, \right], \hat{\kappa}\right] + \ldots$$

for the first few terms.

16. Show that the dressed vacuum contaions undressed pairs: evaluate the first few terms of N^e and N^p. Show that $N^e = N^p$.

17. Verify the commutator expressions for the X operators.

18. Show that time-reversal symmetry reduces the number of 2-electron integrals by a factor of 4 for all classes of integrals (i.e. numbers of bars).

19. Verify the reduction from the general Fock matrix to the closed-shell Fock matrix.

20. Verify the expression for the scalar Fock matrix using the transformations from the 2-spinor basis.

21. Verify the quaternionic unitary transformation. What happens if the operator is antisymmetric under time-reversal?

22. Verify the symmetry of the 2-spinor 2-particle wave functions by substitution and expansion.

23. Verify the Dirac relation $(\boldsymbol{\sigma} \cdot \mathbf{u})(\boldsymbol{\sigma} \cdot \mathbf{v}) = \mathbf{u} \cdot \mathbf{v} + i\boldsymbol{\sigma} \cdot \mathbf{u} \times \mathbf{v}$

24. Derive the operators of the Breit-Pauli Hamiltonian from the modified Dirac Hamiltonian, i.e. with the assumption that $\Phi^L = \Psi^L$.