

Theoretische Physik 4 (Quantentheorie)

Sommersemester 2014

Übungsblatt 11

Aufgabe 11.1: Zeitunabhängige StörungstheorieSei H_0 der Hamiltonoperator des harmonischen Oszillators,

$$H_0 = \hbar\omega \left(-\frac{d^2}{d\xi^2} + \frac{1}{4}\xi^2 \right), \quad (1)$$

und sei $H = H_0 + \lambda H_1$ mit

$$H_1 = e^{-\xi^2/2} (1 - 2\xi^2). \quad (2)$$

Berechnen Sie näherungsweise die Grundzustandsenergie von H für $\lambda \ll \hbar\omega$ mit Störungstheorie.*Hinweis:*

$$\phi_0^{(0)}(\xi) = (2\pi)^{-1/4} e^{-\xi^2/4}, \quad (3)$$

$$\phi_1^{(0)}(\xi) = (2\pi)^{-1/4} \xi e^{-\xi^2/4}, \quad (4)$$

$$\phi_2^{(0)}(\xi) = (2\pi)^{-1/4} \frac{1}{\sqrt{2}} (\xi^2 - 1) e^{-\xi^2/4}. \quad (5)$$

6 Punkte.

Aufgabe 11.2: Baker-Campbell-Hausdorff-Formel

Zeigen Sie die Baker-Campbell-Hausdorff-Formel

$$e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]} \quad (6)$$

falls $[A, B]$ mit A und mit B vertauscht.*Hinweis:* Ersetzen Sie $A \mapsto tA$ und $B \mapsto tB$ und zeigen Sie die Identität für $t \in \mathbb{R}$.

6 Punkte.

Aufgabe 11.3: Zwei-Elektronen-Atome

Lesen Sie die beigefügten Kopien, und leiten Sie die darin aufgeführten Gleichungen (10.49)–(10.51) (1. Ordnung Störungstheorie) bzw. (10.128)–(10.132) (Variationsverfahren) her.

8 Punkte.

Abgabe am 08.07.2014 vor Beginn der Vorlesung. Viel Erfolg!

levels mentioned previously. The perturbative series for the n th level is Borel summable, and its Borel sum is $\text{Re } E_n(\lambda)$, and the widths $\Gamma_n(\lambda) \equiv -2\text{Im } E_n(\lambda)$ are positive for almost all values of λ . For the numerical computations of these levels, see [YB 78], [DR 81], [AL 88]. In particular, for the example discussed previously, $E_0(0.2) = 0.968631994 - i1.61204190 \times 10^{-5}$.

10.5 Two-Electron Atoms (II)

Consider now a nucleus of charge $Z|e|$ with two bound electrons. After neglecting the Hughes-Eckart terms (see Sect. 14.1) the Hamiltonian can be decomposed in the form

$$H = H_0 + H_1$$

$$H_0 = \sum_{i=1}^2 \left[-\frac{\hbar^2}{2\mu} \Delta_i - \frac{Ze^2}{r_i} \right] \equiv \sum_i H_{0i}, \quad H_1 = \frac{e^2}{r_{12}}, \quad (10.46)$$

where r_1 and r_2 are the position vectors of the two electrons, $r_{12} = |r_1 - r_2|$ and μ is the reduced mass of an electron with respect to the nucleus. In the ground state of H_0 the two electrons occupy $1s$ states (with antiparallel spins to ensure the total antisymmetry of the combined states for two identical fermions, Sect. 13.2), and therefore the unperturbed ground state is non-degenerate and has energy

$$E_0^{(0)} = -\mu(Z\alpha c)^2. \quad (10.47)$$

Its normalized wave function is

$$\psi_0^{(0)}(r_1, r_2) = (\pi a^3)^{-1} e^{-(r_1+r_2)/a}, \quad (10.48)$$

where $a = \hbar/\mu(Z\alpha c)$. The first correction to the energy in perturbation theory is

$$E_0^{(1)} = \frac{e^2}{\pi^2 a^6} \int d^3 r_1 d^3 r_2 \frac{1}{r_{12}} e^{-2(r_1+r_2)/a}. \quad (10.49)$$

Taking into account (A.135) and (A.41) the angular integrations can be performed immediately yielding

$$E_0^{(1)} = \frac{16e^2}{a^6} \int_0^\infty dr_1 r_1^2 \times \left[\int_0^{r_1} dr_2 \frac{r_2^2}{r_1} e^{-2(r_1+r_2)/a} + \int_{r_1}^\infty dr_2 r_2 e^{-2(r_1+r_2)/a} \right]. \quad (10.50)$$

A further elementary integration gives $E_0^{(1)} = 5\mu(Z\alpha c)^2/8Z$; thus, to first order in perturbation theory the energy of the ground state is given by

$$E_{\text{pert}} = -\mu(Z\alpha c)^2 \left(1 - \frac{5}{8Z} \right). \quad (10.51)$$

Table 10.3 contains the values of the energies (10.51) and those computed using the variational method (see Sect. 10.10) for various atoms. The experimental data are extracted from [KU 62]. It is to be expected that as Z increases, the Coulomb repulsion energy between the two electrons should become relatively smaller than the interaction energy between the electrons and the nucleus, the perturbative corrections should be less important, and the agreement between theory and experiment should improve. This is clearly the case in Table 10.3.

Table 10.3. Comparison between E_{pert} and the experimental value. For atoms we use the spectroscopic notation. The roman numeral indicates the number of electrons removed, plus one. All values are given in eV

Atom	$-E_0^{(0)}$	$E_0^{(1)}$	$-E_{\text{pert}}$	$-E_{\text{var}}$	$-E_{0,\text{exp}}$
He	108.831 68 (36)	34.01	74.82	77.48	79.003 49 (58)
Li II	244.885 72 (82)	51.02	193.87	196.52	198.083 8 (31)
Be III	435.359 9 (14)	68.02	367.33	369.99	371.574 (12)
B IV	680.257 4 (22)	85.03	595.22	597.88	599.502 (25)
C V	979.574 6 (32)	102.04	877.19	880.19	881.885 (37)
N VI	1 333.318 8 (44)	119.05	1 214.27	1 216.93	1 218.741 (62)
O VII	1 741.486 0 (58)	136.05	1 605.09	1 608.09	1 610.068 (74)
F VIII	2 204.080 2 (72)	153.06	2 051.02	2 053.67	2 055.909 (99)

For the computation of higher order perturbative corrections, there are mixed techniques incorporating both perturbation theory and variational methods initially proposed by *Hylleraas* [HY 30]. In [MI 65] one can find the coefficients e_n of the perturbative expansion

$$E_0 = -\mu(Z\alpha c)^2 \sum_{n=0}^{\infty} e_n Z^{-n} \quad (10.52)$$

for $n \leq 21$. For instance

$$e_0 = 1, \quad e_1 = -\frac{5}{8}$$

$$e_2 = 0.1576666428,$$

$$e_3 = -0.008699029,$$

$$e_4 = 0.000888705,$$

$$e_5 = 0.001036374. \quad (10.53)$$

The sum of this perturbative series truncated at $n = 21$ reproduces the experimental results with a precision of the order of 10^{-4} , and one should not expect an improvement of this result, because the terms neglected in the Hamiltonian (Hughes-Eckart, relativistic corrections etc.) start making contributions at this level of accuracy.

which is the inequality mentioned. In its applications it suffices to have a lower bound estimate of \bar{E} .

For example, let H be the Hamiltonian (10.28) for the anharmonic oscillator in units $2M = \hbar = k/2 = 1$. Taking for ϕ the ground state $\psi_0^{(0)}$ of the harmonic oscillator (10.29), a simple computation leads to

$$\langle H \rangle_\phi = 1 + \frac{3}{4}\lambda, \quad \Delta_\phi^2 H = 6\lambda^2 \quad (10.123)$$

and therefore, Temple's inequality becomes

$$1 + \frac{3}{4}\lambda - \frac{1}{\bar{E}(\lambda) - (1 + 3\lambda/4)} \leq E_0(\lambda), \quad \text{if } 1 + \frac{3}{4}\lambda < \bar{E}(\lambda). \quad (10.124)$$

Since the perturbation λx^4 is repulsive ($\lambda \geq 0$) and even, restricting ourselves to the even parity subspace we can take $\bar{E}(\lambda) \geq E_2(0) = 5$, so that

$$1 + \frac{3}{4}\lambda - \frac{6\lambda^2}{4 - 3\lambda/4} \leq E_0(\lambda), \quad 0 \leq \lambda \leq \frac{16}{3}. \quad (10.125)$$

The upper bound $\langle H \rangle_\phi = 1 + 3\lambda/4 \geq E_0(\lambda)$ can easily be improved with little extra effort if we apply the Rayleigh-Ritz method with $D_2 = \{\psi_0^{(0)}, \psi_2^{(0)}\}$, i.e., the space spanned by the first two even eigenvectors of the harmonic oscillator. The matrix representing H in D_2 is

$$H_{D_2} = \begin{pmatrix} 1 + \frac{3}{4}\lambda & \frac{3}{\sqrt{2}}\lambda \\ \frac{3}{\sqrt{2}}\lambda & 5 + \frac{3}{4}\lambda \end{pmatrix}, \quad (10.126)$$

whose lowest eigenvalue gives an upper bound on $E_0(\lambda)$ better than $1 + 3\lambda/4$. Thus, for $\lambda = 0.2$ we obtain, using (10.125) and (10.126): $1.08766 \leq E_0(0.2) \leq 1.11913$, to be compared with the exact value $E_0(0.2) = 1.11829$.

For more sophisticated methods (intermediate Hamiltonians, projection techniques, etc.), of great utility in atomic and molecular physics, see [WS 72], [GH 78], [TH 81].

10.10 Two-Electron Atoms (II)

The problem of computing the ground state energy for a nucleus of charge $Z|e|$ with two bound electrons, treated in Sect. 10.5 from the point of view of perturbation theory, will be analyzed here using the variational method. The Hamiltonian appears in (10.46), and if the interaction terms were absent, the space part of the wave function for the ground state 1^1S_0 (in the notation $n^{2S+1}L_J$, $n =$ order of the level) is

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = (\pi a^3)^{-1} e^{-(r_1+r_2)/a}, \quad (10.127)$$

where $a = \hbar/\mu(Z\alpha c)$. We can take (10.127) as a family of trial functions, leaving a as an arbitrary parameter. It is straightforward to obtain

$$\begin{aligned} \langle \psi | -\frac{1}{2\mu} \Delta_1 | \psi \rangle &= \langle \psi | -\frac{1}{2\mu} \Delta_2 | \psi \rangle = \frac{1}{2\mu a^2}, \\ \langle \psi | -\frac{Ze^2}{r_1} | \psi \rangle &= \langle \psi | -\frac{Ze^2}{r_2} | \psi \rangle = -\frac{Ze^2}{a}. \end{aligned} \quad (10.128)$$

On the other hand we know from Sect. 10.5 that

$$\langle \psi | \frac{1}{r_{12}} | \psi \rangle = \frac{5}{8a}, \quad (10.129)$$

Since $|\psi\rangle$ is normalized, the expectation value of the energy is

$$\langle \psi | H | \psi \rangle = \mu(\alpha c)^2 Z' [Z' - 2Z + \frac{5}{8}]. \quad (10.130)$$

with $Z' \equiv \hbar/\mu\alpha(\alpha c)$. Expression (10.130) has a minimum at $Z' = Z - 5/16$, indicating the extent to which one electron sees the nucleus screened by the other. For the ground state energy we obtain the inequality

$$E_0 \leq E_{\text{var}} = -\mu(Z\alpha c)^2 \left(1 - \frac{5}{16Z}\right) \quad (10.131)$$

and comparing this result with (10.51),

$$E_{\text{pert}} = E_{\text{var}} + \frac{25}{256} \mu(\alpha c)^2 = E_{\text{var}} + 2.6573879(88) \frac{\mu}{m_e} \text{ eV}. \quad (10.132)$$

It is therefore clear, in this case, that the variational computation gives a better approximation to the energy than the first order of perturbation theory (see Table 10.3).

To improve the agreement between theory and experiment it suffices in principle to choose a wider family of trial functions [HY 30]. Notice first of all that in the sector 1^1S_0 the Hamiltonian H has some level with an energy smaller than E_{var} given in (10.131). Moreover, in any other sector 2^S+1L_J the positivity of the perturbation implies that the energy is larger than $-(5/8)\mu(Z\alpha c)^2$. Hence, the ground state will be in the sector 1^1S_0 as long as $Z > 1.50$, and to compute it, we can restrict its variational search to functions symmetric under the exchange $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$ and spin singlet. The electrostatic repulsion between the electrons induces a correlation in their positions which is not incorporated in the choice (10.127). Functions often used including these features are

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = (\pi a^3)^{-1} e^{-(r_1+r_2)/a} [1 + Af(r_1, r_2, r_{12})]. \quad (10.133)$$

Sometimes these trial functions depend on hundreds of parameters [KI 57], [PE 62]. With them it has been possible to obtain excellent variational estimates and rather sharp lower bounds. For example, it is known that for He in