

Lecture 7: Stationary Perturbation Theory

In most practical applications the time independent Schrödinger equation

$$H\psi = E\psi \tag{1}$$

cannot be solved exactly and one has to resort to some scheme of finding approximate solutions, preferably by some method of iteration that allows one, at least in principle, to find the solution with any desired accuracy. One of the most widely used such methods is perturbation theory.

Perturbation theory is applicable if there is a possibility of separating the Hamiltonian H into a sum of H_0 , say, for which one is able to find the exact solution of the corresponding Schrödinger equation, and a term H' , the *perturbation*. The latter term must be in some sense small for the method to work. The precise meaning of the smallness needed to make the method useful has to be investigated in each case separately. However, in order to have a general picture of this meaning one could think of the energy levels of a hydrogen atom perturbed by some external force: if the shift of the energy levels is small compared with their separation in the unperturbed state, then perturbation theory will be applicable.

1. The non-degenerate case

Perturbation theory proceeds somewhat differently in the presence or in the absence of degeneracy. We shall consider in this section only the case of non-degenerate perturbation theory. This will allow us to apply the method to most one-dimensional cases. Three-dimensional systems will usually have some degree of degeneracy; this will be taken into account in the next section.

Thus we assume that the Hamiltonian can be written in the form

$$H = H_0 + \lambda V \tag{2}$$

where I have written λV for H' . The parameter λ can be thought of as some quantity which can be varied at will and can be reduced to zero, in which case the perturbation disappears and all results must revert to the unperturbed case. If we consider the case of a hydrogen spectrum which we observe with the atom placed in a magnetic field (Zeeman effect) or in an electric field (Stark effect), then λ can be thought of as characterising the strength of the field over which we have complete control.

The unperturbed Hamiltonian H_0 is supposed to have been chosen such that the solution of the corresponding Schrödinger equation is known: ¹

$$H_0\phi_n = E_n^{(0)}\phi_n \tag{3}$$

with known eigenvalues $E_n^{(0)}$ and known eigenfunctions ϕ_n which form a complete set of orthonormal functions:

$$(\phi_m, \phi_n) = \delta_{mn}. \tag{4}$$

¹The notation used here suggests the presence of discrete levels only. The modifications to include continuous states are straightforward (see, e.g. L.I. Schiff, Quantum Mechanics).

Before actually applying perturbation theory we shall rewrite the Schrödinger equation in the form of a matrix equation. This can be done by using the completeness of the set $\{\phi_n\}$ to express the n th eigenfunction of H in the form

$$\psi_n = \sum_k c_{nk} \phi_k. \quad (5)$$

Here the expansion coefficients are functions of λ : we must have

$$c_{nk} = \delta_{nk} \quad \text{for } \lambda = 0 \quad (6)$$

to ensure that $\psi_n = \phi_n$ for $\lambda = 0$.

If we now substitute (5) into (1) and take the scalar product with ϕ_m , then we get

$$(E_n - E_m^{(0)})c_{nm} = \lambda \sum_k c_{nk} V_{mk} \quad (7)$$

where $V_{mk} = (\phi_m, V\phi_k)$. Equation (7) is the Schrödinger equation in matrix form and is equivalent to Eq. (1). Mathematically it is a linear simultaneous equation with the expansion coefficients c_{nm} and the energy eigenvalue E_n as the unknown quantities. If the system under consideration had only a small number of energy levels one could solve this equation without any approximations by standard methods of linear algebra.

Exercise: Assuming that the system under consideration has only two energy levels, show that the eigenvalues are

$$E_{1,2} = \frac{1}{2}(H_{11} + H_{22}) \pm \sqrt{\frac{1}{4}(H_{11} + H_{22})^2 + |H_{12}|^2}$$

where $H_{mn} = (\phi_m, H\phi_n)$.

In most cases of practical interest the number of eigenstates is large or even infinite. Then the exact solution of Eq. (7) becomes either impractical or impossible. In these cases it may be possible to find the solution by iteration using perturbation theory.

The essence of perturbation theory is to expand the energy eigenvalue and the eigenfunction into a power series in λ ²

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (8a)$$

$$c_{nk} = \delta_{nk} + \lambda c_{nk}^{(1)} + \lambda^2 c_{nk}^{(2)} + \dots \quad (8b)$$

Note that Eq. (8b) is equivalent with

$$\psi_n = \phi_n + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots \quad (8c)$$

²Many authors, e.g. P.A.M. Dirac, *The Principles of Quantum Mechanics*, do not use such an expansion parameter but assume each successive term to be of smaller order than the preceding term. L.I. Schiff, *Quantum Mechanics*, uses an expansion parameter λ but does not associate with it any physical significance: it appears as an auxiliary variable which is set equal to one at the end of the calculation. It is strongly recommended to study the approaches taken by different authors to see how many different ways lead to the same result.

where $\psi_n^{(i)} = \sum_k c_{nk}^{(i)} \phi_k$, $i = 1, 2, \dots$

Substitution of Eqs. (8) into (7) yields

$$\begin{aligned} (E_n^{(0)} - E_m^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) &\times (\delta_{nm} + \lambda c_{nm}^{(1)} + \lambda^2 c_{nm}^{(2)} + \dots) \\ &= \lambda \sum_k (\delta_{nk} + \lambda c_{nk}^{(1)} + \lambda^2 c_{nk}^{(2)} + \dots) V_{mk} \end{aligned}$$

and comparing powers of λ we get the following set of equations:

$$(E_n^{(0)} - E_m^{(0)}) \delta_{nm} = 0 \quad (9a)$$

$$(E_n^{(0)} - E_m^{(0)}) c_{nm}^{(1)} + E_n^{(1)} \delta_{nm} = V_{mn} \quad (9b)$$

$$(E_n^{(0)} - E_m^{(0)}) c_{nm}^{(2)} + E_n^{(1)} c_{nm}^{(1)} + E_n^{(2)} \delta_{nm} = \sum_k c_{nk}^{(1)} V_{mk} \quad (9c)$$

$$(E_n^{(0)} - E_m^{(0)}) c_{nm}^{(3)} + E_n^{(1)} c_{nm}^{(2)} + E_n^{(2)} c_{nm}^{(1)} + E_n^{(3)} \delta_{nm} = \sum_k c_{nk}^{(2)} V_{mk} \quad (9d)$$

etc. Equation (9a) contains no new information: it is the statement that $E_m^{(0)} \neq E_n^{(0)}$ for $m \neq n$.

From Eq. (9b) we get $E_n^{(1)}$ by putting $m = n$:

$$\boxed{E_n^{(1)} = V_{nn}} \quad (10)$$

and we get $c_{nm}^{(1)}$ by putting $m \neq n$:

$$\boxed{c_{nm}^{(1)} = \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} \quad (m \neq n)} \quad (11)$$

The coefficient $c_{nn}^{(1)}$ remains undefined by Eqs. (9) and will be chosen by the requirement that the function $\psi_n = \phi_n + \lambda \psi_n^{(1)}$ be normalised to the 1st order in λ . Thus, using Eqs. (8) and (4), we get

$$(\psi_n, \psi_n) = (\phi_n, \phi_n) + \lambda [(\psi_n^{(1)}, \phi_n) + (\phi_n, \psi_n^{(1)})] + O(\lambda^2) = 1 + \lambda(c_{nn} + c_{nn}^*) + O(\lambda^2) = 1$$

and it is evidently sufficient to put

$$\boxed{c_{nn}^{(1)} = 0} \quad (11')$$

to ensure the normalisation of ψ_n to 1st order in λ . This completes the solution of Eq. (1) to first order of perturbation theory.

To find the 2nd order corrections we use Eq. (9c). Setting $m = n$ and using Eqs. (11) we get

$$\boxed{E_n^{(2)} = \sum_{k \neq n} \frac{V_{kn} V_{nk}}{E_n^{(0)} - E_k^{(0)}} = \sum_{k \neq n} \frac{|V_{nk}|^2}{E_n^{(0)} - E_k^{(0)}}} \quad (12)$$

where in the last step we have used the hermiticity of V . The 2nd order correction to the wave function can be found by putting $m \neq n$ in (9c), and having found the 2nd order correction one can proceed to find the 3rd order correction using (9d), *etc.* So, at least in principle the solution can be found to any desired accuracy by successively increasing the number of terms.

An important result of our derivation is that the 1st order correction $E_n^{(1)}$ is linear in the perturbation, the 2nd order correction $E_n^{(2)}$ is quadratic in the perturbation and so on. This

implies at least the possibility that for sufficiently small perturbations the series will converge. However, it happens that even in cases where the perturbation series is known to diverge one gets sometimes good agreement with experimental results if one takes only the lowest order term (cf. P.A.M. Dirac, *Principles of Quantum Mechanics*, Section 42).

We summarise our results by writing down the energy eigenvalue E_n of the perturbed system up to the 2nd order of perturbation theory:

$$E_n = E_n^{(0)} + H'_{nn} + \sum_{k \neq n} \frac{|H'_{nk}|^2}{E_n^{(0)} - E_k^{(0)}} \quad (13)$$

where $H' = \lambda V$ is the perturbation.

Exercise:

1. A one dimensional harmonic oscillator with Hamiltonian $\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2$ is perturbed by an additional potential energy λx . Find the energy eigenvalues to second order in the perturbation, given the eigenvalues of the energy of the unperturbed harmonic oscillator $E_n = \hbar\omega(n + \frac{1}{2})$, and

$$(u_n, xu_k) = \sqrt{\frac{\hbar}{2m\omega}} (\sqrt{n+1} \delta_{k,n+1} + \sqrt{n} \delta_{k,n-1})$$

where $u_n(x)$ are the eigenfunctions of the unperturbed harmonic oscillator.

2. Show that the same result can be obtained without the use of perturbation theory by solving the eigenvalue problem of the perturbed harmonic oscillator exactly.
3. (i) If the harmonic oscillator is perturbed by an additional potential energy $V_1 = gx^3$, discuss the physical justification of using *stationary* perturbation theory to find the perturbed energy levels. What is the lowest value of the total energy at which perturbation theory is certainly going to fail?
 (ii) Assuming that the use of perturbation theory is justified, explain the procedure of calculating the perturbative correction, to which the x^3 term gives rise, in the lowest non-vanishing order.
4. Explain why the use of *stationary* perturbation theory is justified in the case of a perturbation of the harmonic oscillator by $V(x) = ax^3 + bx^4$ and calculate the correction to the energy in the lowest non-vanishing order.

Answer. The energy shift in the lowest non-vanishing order is

$$\frac{3b}{4} \left(\frac{\hbar}{m\omega} \right)^2 (2n^2 + 2n + 1) - \frac{15}{4} a^2 \frac{\hbar^2}{m^3 \omega^4} \left(n^2 - n + \frac{11}{30} \right)$$

Note that this result implies that the correction due to the x^3 term is of 2nd order whereas that due to the x^4 term is of 1st order.

5. Calculate the energy shift of the ground state energy of a hydrogen-like atom (or ion) caused by the finite size of the nucleus, assuming that the charge of the nucleus is uniformly distributed over its volume.

Answer. The P.E. of the electron in the field of a nucleus of charge Ze and radius R , assuming uniform charge distribution, is given by

$$V(r) = \begin{cases} -\frac{Ze^2}{2R} \left(3 - \frac{r^2}{R^2}\right) & r \leq R \\ -\frac{Ze^2}{r} & r \geq R \end{cases}$$

and if we choose the unperturbed Hamiltonian to be $H_0 = \hat{T} + V_c(r)$, with $V_c(r) = -\frac{Ze^2}{r}$, then the ground state eigenfunction of H_0 is the well known hydrogen wave function $\psi_0 = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$, where $a = a_{Bohr}/Z$ and $a_{Bohr} = 5.3 \times 10^{-11}$ m is the Bohr radius.

The corresponding ground state energy is $E_1^{(0)} = -\frac{1}{2}(Z\alpha)^2 m_e c^2$. The perturbation then becomes

$$H' = \begin{cases} V(r) - V_c(r) & \text{for } r \leq R \\ 0 & \text{for } r \geq R \end{cases}$$

The 1st order correction is given by $E_1^{(1)} = (\psi_0, H' \psi_0)$ and we note that the integration over the polar angles gives just a factor of 4π leaving us with the integral over r . This integral can be simplified if one realises that the upper limit of integration is the nuclear radius R which even for the heaviest nuclei does not exceed $\sim 10^{-14}$ m. This implies that over the entire range of r the exponential function is to a good approximation equal to one. The remaining integration is straightforward and yields

$$E_1^{(1)} = 0.8 |E_1^{(0)}| \left(\frac{R}{a}\right)^2$$

Thus for hydrogen one finds $E_1^{(1)}/|E_1^{(0)}| \sim 10^{-9}$, for oxygen ($Z = 8$) one gets $\sim 4 \times 10^{-7}$, and for uranium ($Z = 92$) $\sim 3 \times 10^{-4}$, where for the order-of-magnitude estimates we have used a well known result from nuclear physics, $R = R_0 A^{1/3}$, $R_0 = 1.3 \times 10^{-15}$ m, together with the approximate relation $A \approx 2Z$ between mass number A and atomic number Z .

6. Calculate the shift of the ground state energy of the hydrogen atom in a uniform electric field (Stark effect).

Answer. The perturbation to the Hamiltonian of the hydrogen atom is in this case $H' = e\mathcal{E}z$ if \mathcal{E} is the electric field strength and we assume that the field is in the z direction.

The 1st order correction vanishes by symmetry. The 2nd order correction is given by

$$E_1^{(2)} = \sum_{n>1,lm} \frac{|(\phi_{nlm}, H' \phi_{100})|^2}{E_1^{(0)} - E_n^{(0)}}$$

Recall that the sum has to be extended over the *complete* set of eigenfunctions. In the present case the complete set of eigenfunctions includes the eigenfunctions of the continuum states for which the summation over n must be replaced by an integration

over the energy E . But such a direct approach leads to an intractable mathematical problem. A method that leads to the exact result is described in L.I. Schiff, *Quantum Mechanics*. Evaluation of the above sum gives the result

$$E_1^{(2)} = -2a_{Bohr}^3 \mathcal{E}^2 \sum_{n=2}^{\infty} \frac{n^2}{n^2 - 1} f(n)$$

where $f(n) = \frac{2^8 n^7 (n-1)^{2n-5}}{3 (n+1)^{2n+5}}$. Convergence of the above series is poor and one has to take a large number of terms for a reasonable approximation. Thus one finds

$$E_1^{(2)} = -1.832 a_{Bohr}^3 \mathcal{E}^2$$

which is about 20% too small on account of the neglected continuum states. In spite of the numerical deficiency of our result it is not without interest physically: it tells us that the hydrogen atom in an electric field acquires an induced dipole moment d that is proportional to the external electric field:

$$d = -\frac{\partial E_1^{(2)}}{\partial \mathcal{E}} \approx -4a_{Bohr}^3 \mathcal{E}$$

2. Perturbation theory in the presence of Degeneracy

A problem additional to the one solved in the previous section arises if the energy level, for which we want to calculate the effect of the perturbation, is degenerate. Let us express the degeneracy of the n th level of the unperturbed system by writing the wave functions which correspond to the energy eigenvalue $E_n^{(0)}$ in the form

$$\phi_{n\alpha} \quad \alpha = 1, \dots, f \tag{14}$$

The label α has to be understood in a generic sense. A well known example of degeneracy is found in the stationary states of the hydrogen atom which are characterised by three quantum numbers: the principal quantum number n and the angular momentum quantum numbers l and m . In this case α represents both l and m .

With the above notation the Schrödinger equation of the unperturbed system is

$$\boxed{H_0 \phi_{n\alpha} = E_n^{(0)} \phi_{n\alpha}} \tag{15}$$

and the eigenfunctions form a complete set of orthonormal functions:

$$(\phi_{m\alpha}, \phi_{n\beta}) = \delta_{nm} \delta_{\alpha\beta}. \tag{16}$$

The characteristic novel feature that arises in the case of perturbation of a degenerate level is that the perturbation must be expected to have a different effect on each of the f different states $\phi_{n\alpha}$. Therefore the perturbed energies must also be distinguished by the label α . We

take this into account by writing the perturbation expansions corresponding to Eq. (8) in the form

$$\begin{aligned} E_{n\alpha} &= E_n^{(0)} + \lambda a_{1\alpha} + \lambda^2 a_{2\alpha} + \dots \\ \psi_{n\alpha} &= \psi_{n\alpha}^{(0)} + \lambda \psi_{n\alpha}^{(1)} + \lambda^2 \psi_{n\alpha}^{(2)} + \dots \end{aligned} \quad (17)$$

where for simplicity we have suppressed the label n on the corrections a .

Now, if the perturbation is switched off ($\lambda \rightarrow 0$) then by virtue of Eq. (17) the energy correctly takes on the corresponding value of the unperturbed system, but the wave function becomes $\psi_{n\alpha}^{(0)}$, and *ab initio* we do not know whether this will be any one of the unperturbed states $\phi_{n\alpha}$ or possibly some linear combination of these states. We must therefore consider the most general possibility, namely that

$$\psi_{n\alpha}^{(0)} = \sum_{\beta} c_{\alpha\beta} \phi_{n\beta}. \quad (18)$$

Thus, in the case of degeneracy we have the additional problem to find the superposition coefficients $c_{\alpha\beta}$. We shall now show that this problem is solved automatically together with the problem of finding the 1st order corrections $a_{1\alpha}$.

Let us write down the eigenvalue problem for the Hamiltonian $H = H_0 + \lambda V$ in the form

$$(E_{n\alpha} - H_0)\psi_{n\alpha} = \lambda V\psi_{n\alpha} \quad (19)$$

and substitute the expansions (17). Then we get

$$(E_n^{(0)} - H_0 + \lambda a_{1\alpha} + \dots)(\psi_{n\alpha}^{(0)} + \lambda \psi_{n\alpha}^{(1)} + \dots) = \lambda V(\psi_{n\alpha}^{(0)} + \lambda \psi_{n\alpha}^{(1)} + \dots) \quad (20)$$

and comparing powers of λ we get a set of equations similar to Eqs. (9). The first one of these is again the trivial statement and need not be mentioned any more. Of particular interest in the present case is only the equation that arises from the terms linear in λ :

$$(E_n^{(0)} - H_0)\psi_{n\alpha}^{(1)} + a_{1\alpha}\psi_{n\alpha}^{(0)} = V\psi_{n\alpha}^{(0)}. \quad (21)$$

Taking the scalar product with $\phi_{n\gamma}$ and using Eq. (18) yields

$$\boxed{a_{1\alpha}c_{\alpha\gamma} = \sum_{\beta=1}^f c_{\alpha\beta} V_{\gamma\beta}^{(n)}} \quad (22)$$

where $V_{\gamma\beta}^{(n)} = (\phi_{n\gamma}, V\phi_{n\beta})$, and since α is fixed and γ can take on f different values Eq. (22) represents a system of f simultaneous linear homogeneous equations for the f unknown coefficients $c_{\alpha\beta}$. The 1st order energy shift $a_{1\alpha}$ here plays the role of an eigenvalue. The characteristic equation of (22) is a polynomial of order f in $a_{1\alpha}$ so that we can expect up to f different roots, each root corresponding to one value of α . If all roots are different one says that the degeneracy is completely removed in 1st order. Often the degeneracy is only partly removed in 1st order, *i.e.* not all roots of the characteristic equation are different.

Let us consider in detail the particular case of two-fold degeneracy, $f = 2$. Then Eq. (22) takes on the form

$$\begin{aligned} a_{1\alpha}c_{\alpha 1} &= V_{11}c_{\alpha 1} + V_{12}c_{\alpha 2} \\ a_{1\alpha}c_{\alpha 2} &= V_{21}c_{\alpha 1} + V_{22}c_{\alpha 2} \end{aligned} \quad (23)$$

which has the characteristic equation

$$a_{1\alpha}^2 - T a_{1\alpha} + \Delta = 0$$

where T and Δ are the trace and the determinant of the matrix $V_{\alpha\beta}$, respectively:

$$T = (V_{11} + V_{22}), \quad \Delta = V_{11}V_{22} - V_{12}V_{21}$$

The two roots of the characteristic equation are

$$a_{1\alpha} = \frac{1}{2}T \pm \sqrt{\left(\frac{1}{2}T\right)^2 - \Delta}.$$

Thus the degeneracy is removed in 1st order unless $T^2 - 4\Delta = 0$. The separation of the split energy levels is given by

$$\Delta a_1 \equiv a_{1+} - a_{1-} = \sqrt{(V_{11} - V_{22})^2 + 4|V_{12}|^2}.$$

The split energy levels correspond to the zeroth-order wave functions

$$\psi_{\pm} = c_{1\pm}\phi_1 + c_{2\pm}\phi_2$$

where the coefficients must be found from the simultaneous equations

$$\begin{aligned} (V_{11} - a_1)c_1 + V_{12}c_2 &= 0 \\ V_{12}c_1 + (V_{22} - a_1)c_2 &= 0 \end{aligned}$$

together with the normalisation condition

$$|c_1|^2 + |c_2|^2 = 1.$$

After straightforward if somewhat tedious algebra one can get the coefficients in the following form:

$$\begin{aligned} c_{1\pm} &= \left\{ \frac{V_{12}}{2|V_{12}|} \left[1 \pm \frac{V_{11} - V_{22}}{\sqrt{(V_{11} - V_{22})^2 + 4|V_{12}|^2}} \right] \right\}^{1/2} \\ c_{2\pm} &= \pm \left\{ \frac{V_{21}}{2|V_{12}|} \left[1 \mp \frac{V_{11} - V_{22}}{\sqrt{(V_{11} - V_{22})^2 + 4|V_{12}|^2}} \right] \right\}^{1/2} \end{aligned}$$

Note that only the relative phase between $c_{1\pm}$ and $c_{2\pm}$ is fixed by the simultaneous equations; the overall phase is arbitrary and was chosen such as to give the resulting formulæ a particularly symmetric form.

Exercise: Calculate the splitting of the 1st excited state of the hydrogen atom in a uniform electric field in 1st order of degenerate perturbation theory (Stark effect).

Answer. The 1st excited state corresponds to the principal quantum number $n = 2$; there are four degenerate states with angular momentum quantum numbers $l = 0, 1, m = -l, -l+1, \dots, l$.

The characteristic equation is a quartic equation in the 1st order energy correction which must be computed from a 4×4 determinant. This seems a rather tedious task. However, with a few very general considerations one can see that there is only one non-zero matrix element: $V_{01} = -3e\mathcal{E}a_{Bohr}$, and that the characteristic equation reduces to the simple form

$$a_1^2(a_1^2 - |V_{01}|^2) = 0$$

whose four roots are $0, 0$, and $\pm |V_{01}|$. Thus there is one two-fold degenerate unshifted level and two non-degenerate levels shifted by equal amounts up and down. The wave function corresponding to the upper level is $(\phi_{200} - \phi_{210})/\sqrt{2}$, and the wave function of the lower level is $(\phi_{200} + \phi_{210})/\sqrt{2}$; the unshifted state remains some linear superposition of the states ϕ_{211} and ϕ_{21-1} .

To derive these results consider the general matrix element $(\phi_{2lm}, V\phi_{2l'm'})$ where the perturbation Hamiltonian is $V = e\mathcal{E}z$. This Hamiltonian has cylindrical symmetry about the z axis and therefore commutes with the angular momentum operator L_z .³ Thus

$$(\phi_{2lm}, [L_z, V]\phi_{2l'm'}) = \hbar(m - m')(\phi_{2lm}, V\phi_{2l'm'}) = 0,$$

i.e.

$$(\phi_{2lm}, V\phi_{2l'm'}) = 0 \quad \text{unless} \quad m - m' = 0.$$

Next we note that

$$(\phi_{2lm}, V\phi_{2lm}) = 0$$

by parity, which leaves only the matrix elements $(\phi_{2lm}, V\phi_{2l'm'})$ with $l' \neq l$ to calculate. But there are only two matrix elements: V_{01} and V_{10} , and they are related by Hermiticity of the Hamiltonian: $V_{01} = V_{10}^*$, *i.e.* effectively we need to evaluate only the matrix element V_{01} . To do this we must substitute the hydrogen wave functions $\psi_{200}(r, \theta, \phi) = R_{20}(r)Y_{00}(\theta, \phi)$ and $\psi_{210}(r, \theta, \phi) = R_{21}(r)Y_{10}(\theta, \phi)$ and carry out the integrations, hence

$$\begin{aligned} V_{01} &= e\mathcal{E} \int d^3r R_{20}(r)Y_{00}(\theta, \phi)zR_{21}(r)Y_{10}(\theta, \phi) \\ &= -3e\mathcal{E}a_{Bohr}. \end{aligned}$$

³Formally one can see this by noting that $z = r \cos \theta$ and $L_z = -i\hbar \partial/\partial \phi$.