

# Stark Effect

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## Abstract

An external electric field  $\mathbf{E}$  polarizes a hydrogen atom. This lowers the ground state energy and also partly breaks the  $N^2$ -fold degeneracy of the  $N^2$  hydrogenic states  $\psi_{NLM}(\mathbf{x}) = \langle \mathbf{x} | NLM \rangle$  with principal quantum number  $N$ . We apply the tools of nondegenerate state perturbation theory to describe the effect of the field  $\mathbf{E}$  on the bound states of the hydrogen atom.

## 1 Introduction

An electric field partly lifts the degeneracies of atomic energy levels. This splitting was observed by Stark [1] and explained by Schrödinger [2]. We compute the Stark effect on atomic hydrogen using perturbation theory by diagonalizing the perturbation term in the  $N^2$ -fold degenerate multiplet of states with principal quantum number  $N$ . We exploit the symmetries of this problem to simplify the numerical computations. In particular, after assuming the  $N'-N$  matrix elements of the hamiltonian  $\langle N'L'M' | \mathcal{H} | NLM \rangle$  are not important when  $N' \neq N$ , we use symmetry to show that these matrix elements: (i.) vanish unless  $M' = M$ ; (ii.) vanish unless  $L' = L \pm 1$ ; (iii.) are the same for  $M$  and  $-M$ ; and (iv.) factor into a product of two simpler functions which are simple look-ups. The Stark effect partly breaks the  $N^2$ -fold degeneracy of the states in the principal quantum level  $N$  into one  $N$ -fold degenerate multiplet and two multiplets with degeneracies  $k$ , where  $k = 1, 2, \dots, N-1$ . The splitting is indicated in Fig. 1 for  $N = 4$ .

The perturbing hamiltonian is introduced in Sect. 2. In Sect. 3 we construct the appropriate matrix elements of this hamiltonian. The effects of symmetry on this computation are described in Sect. 5 and applied to the 16-fold degenerate multiplet with  $N = 4$  in Sect. 5. The nature of the splitting for arbitrary  $N$  is described in Sect. 6. In a sense, the splitting is similar to that encountered in the case of an external magnetic field  $\mathbf{B}$  (Zeeman effect). In Sect. 12 we apply nondegenerate state perturbation theory to study the effect of the electric field on the ground state of the hydrogen atom. In this case first order perturbation theory provides a null result, and we must go to second order perturbation theory to estimate the atomic polarizability of atomic hydrogen in the ground state. In Sects. 10 and 11 we return to the question of how good is the first approximation that was made: that the  $N'-N$  matrix elements could be neglected. It turns out to be a good approximation in one way, but bad in an unexpected way. We summarize our results in the closing Section.

## 2 Perturbing Hamiltonian

The hydrogen atom interacts with a static external electric field  $\mathbf{E}$  through an electric dipole interaction. This has the form

$$\mathcal{H}_{\text{pert}} = -e\mathbf{E} \cdot \mathbf{r} \quad (1)$$

Here  $e$  is the electron charge ( $e = -|e|$ ) and  $\mathbf{r}$  is the displacement of the electron from the proton.

### 3 Matrix Elements of the Perturbing Hamiltonian

The energy levels of the hydrogen atom are computed by diagonalizing the total Hamiltonian. We do this in the basis of eigenstates of the unperturbed Hamiltonian:

$$\langle N'L'M' | \mathcal{H} + \mathcal{H}_{\text{pert}} | NLM \rangle = E_N \delta_{N'N} \delta_{L'L} \delta_{M'M} + \langle N'L'M' | \mathcal{H}_{\text{pert}} | NLM \rangle \quad (2)$$

Unperturbed states with the same principle quantum number  $N$  are degenerate in energy in the nonrelativistic Schrödinger equation for the hydrogen atom (neglecting all other perturbations). As a result, we must diagonalize the perturbation within each  $N$  multiplet before applying the standard machine of perturbation theory, which has been developed for nondegenerate states.

We make the approximation that the diagonalizations can be carried out within each  $N$  multiplet independently. The validity of this assumption will be discussed in Sects. 8 and 9. As a result of this assumption it is necessary to construct the matrix elements

$$\langle NL'M' | (-e\mathbf{E} \cdot \mathbf{r}) | NLM \rangle \quad (3)$$

and then to carry out the diagonalization of this  $N^2 \times N^2$  matrix.

### 4 Symmetry Reduces Computational Complexity

The calculation is simplified by choosing our coordinate axes carefully. To this end we choose the  $z$  axis in the direction of the electric field  $\mathbf{E}$ . In this coordinate system  $-e\mathbf{E} \cdot \mathbf{r} = |eE|z$ . Next, we replace  $|\mathbf{E}| \rightarrow E$  and  $z = r \cos(\theta) = \sqrt{\frac{4\pi}{3}} r Y_0^1(\theta, \phi)$ . The matrix elements to be computed are

$$\langle NL'M' | -e\mathbf{E} \cdot \mathbf{r} | NLM \rangle = |eE| \int_0^\infty R_{NL'}(r) r R_{NL}(r) dr \times \sqrt{\frac{4\pi}{3}} \int_\Omega Y_{M'}^{L'*}(\Omega) Y_0^1(\Omega) Y_M^L(\Omega) d\Omega \quad (4)$$

The angular integral provides useful selection rules.

**First:**  $\Delta M = 0$  by azimuthal  $[SO(2)]$  symmetry.

**Second:**  $\Delta L = \pm 1, 0$  by rotational  $[SO(3)]$  symmetry.

**Third:** The matrix elements with  $\Delta L = 0$  are zero by reflection symmetry.

The only relevant integral is therefore

$$\mathcal{A}(L \leftrightarrow L - 1, M) = \sqrt{\frac{4\pi}{3}} \int_\Omega Y_{M'}^{L'*}(\Omega) Y_0^1(\Omega) Y_M^{L-1}(\Omega) d\Omega = \delta_{M'M} \sqrt{\frac{(L+M)(L-M)}{(2L+1)(2L-1)}} \quad (5)$$

with  $1 \leq L \leq N - 1$ . It is useful to observe that the integrals are unchanged under  $M \rightarrow -M$  (time-reversal symmetry).

The radial integral is

$$\mathcal{R}(N, L \leftrightarrow L - 1) = \int_0^\infty R_{N,L}(r) r R_{N,L-1}(r) dr = -\frac{3}{2} a_0 N \sqrt{(N+L)(N-L)} \quad (6)$$

Here  $a_0$  is the Bohr radius of the hydrogen atom and  $L$  is again in the range:  $1 \leq L \leq N - 1$ .

For the  $N = 3$  multiplet the  $9 \times 9$  matrix to be diagonalized has the structure

$$\left[ \begin{array}{c|c|c} & * & \\ \hline & & * \\ * & & * \\ \hline & & * \\ * & & \\ & * & \\ & * & \\ & & * \end{array} \right] \begin{array}{c} 0 \quad 0 \\ \hline 1 \quad +1 \\ 1 \quad 0 \\ \hline 1 \quad -1 \\ 2 \quad +2 \\ 2 \quad +1 \\ 2 \quad 0 \\ 2 \quad -1 \\ 2 \quad -1 \end{array} \quad (7)$$

The two columns on the right provide information about the  $L$  and  $M$  values defining the rows and columns of this matrix. The non zero matrix elements are indicated by \*, all other matrix elements are zero.

What this result makes clear is that the matrix can be rewritten as the direct sum of a number of smaller matrices, each identified by different values of the magnetic quantum number  $M$ :

$$\left[ \begin{array}{c|c|c|c|c} & & & & \\ & * & & & \\ * & & & & \\ \hline & & * & & \\ & & * & * & \\ & & * & & \\ \hline & & & & * \\ & & & * & \\ \hline & & & & \\ & & & & \end{array} \right] \begin{array}{c} 2 \quad +2 \\ \hline 1 \quad +1 \\ 2 \quad +1 \\ \hline 0 \quad 0 \\ 1 \quad 0 \\ 2 \quad 0 \\ \hline 1 \quad -1 \\ 2 \quad -1 \\ 2 \quad -2 \end{array} \quad (8)$$

This matrix has been transformed to block-diagonal form. For each value of  $M$  there is an  $(N-|M|) \times (N-|M|)$  block matrix along the diagonal with basis vectors  $| \begin{smallmatrix} L \\ M \end{smallmatrix} \rangle, L = |M|, |M| + 1, \dots, N - 1$ . Furthermore, the matrices associated with  $M$  and  $-M$  are identical. Diagonalization of either provides the spectrum of eigenvalues and eigenvectors for both. For the  $N = 3$  multiplet it is only necessary to

compute one matrix element for a  $2 \times 2$  matrix and two for the  $3 \times 3$  matrix. Then it is necessary to diagonalize the  $3 \times 3$  matrix and one  $2 \times 2$  matrix to compute all eigenvalues and eigenstates. The  $1 \times 1$  matrices are already diagonal. The ingredients for these matrix elements are:

$$\mathcal{R}(3, L \leftrightarrow L - 1) = \frac{1}{a_0} \int_0^\infty R_{3,L}(r)rR_{3,L-1}(r)dr = \begin{array}{cc} L = & 2 \leftrightarrow 1 \quad 1 \leftrightarrow 0 \\ \frac{3}{2} \cdot 3 \cdot \sqrt{5 \cdot 1} & \frac{3}{2} \cdot 3 \cdot \sqrt{4 \cdot 2} \end{array} \quad (9)$$

$$\mathcal{A}(2 \leftrightarrow 1, \pm 1) = \sqrt{\frac{3 \cdot 1}{5 \cdot 3}} \quad \mathcal{A}(2 \leftrightarrow 1, 0) = \sqrt{\frac{2 \cdot 2}{5 \cdot 3}} \quad \mathcal{A}(1 \leftrightarrow 0, 0) = \sqrt{\frac{1 \cdot 1}{3 \cdot 1}} \quad (10)$$

## 5 $N = 4$

The  $N = 3$  case is almost too simple to compute. We therefore carry out the computations for the  $N = 4$  multiplet. In this multiplet there is a total of 16 states  $|4LM\rangle$ , with  $L = 0, 1, 2, 3$  and for each  $L$ ,  $-L \leq M \leq L$ . There is nominally a total of  $16^2 = 256$  matrix elements to compute, of which most are zero (by symmetry) and the rest are simply related to each other (by symmetry).

Each matrix element is a product of two factors: a radial factor and an angular factor. We list these factors below. The radial factor is obtained by evaluating Eq.(6)

$$\mathcal{R}(4, L \leftrightarrow L-1) = \frac{1}{a_0} \int_0^\infty R_{4,L}(r)rR_{4,L-1}(r)dr = \begin{array}{ccc} L = & 3 \leftrightarrow 2 & 2 \leftrightarrow 1 & 1 \leftrightarrow 0 \\ & \frac{3}{2} \cdot 4 \cdot \sqrt{7 \cdot 1} & \frac{3}{2} \cdot 4 \cdot \sqrt{6 \cdot 2} & \frac{3}{2} \cdot 4 \cdot \sqrt{5 \cdot 3} \end{array} \quad (11)$$

and the angular factor is obtained by evaluating Eq.(5).

$$\mathcal{A}(L \leftrightarrow L-1, M) = \sqrt{\frac{(L+M)(L-M)}{(2L+1)(2L-1)}} \begin{array}{ccc} & & M \\ & & \pm 2 & \pm 1 & 0 \\ L & 3 \leftrightarrow 2 & \sqrt{\frac{5 \cdot 1}{7 \cdot 5}} & \sqrt{\frac{4 \cdot 2}{7 \cdot 5}} & \sqrt{\frac{3 \cdot 3}{7 \cdot 5}} \\ & 2 \leftrightarrow 1 & & \sqrt{\frac{3 \cdot 1}{5 \cdot 3}} & \sqrt{\frac{2 \cdot 2}{5 \cdot 3}} \\ & 1 \leftrightarrow 0 & & & \sqrt{\frac{1 \cdot 1}{3 \cdot 1}} \end{array} \quad (12)$$

These  $3+6 = (N-1) + \frac{1}{2}N(N-1) = \frac{1}{2}(N-1)(N+2)$  input data are used to construct the  $4 \times 4$ ,  $3 \times 3$  and  $2 \times 2$  matrices associated with  $M = 0$ ,  $M = \pm 1$ , and  $M = \pm 2$  for the  $N = 4$  multiplet.

For the 4 states with  $M = 0$  we construct the matrix of the perturbation hamiltonian:

$$M = 0 \quad \frac{3}{2} \times eEa_0 \times \begin{bmatrix} 0 & 4 \cdot \sqrt{5 \cdot 3} \sqrt{\frac{1 \cdot 1}{3 \cdot 1}} & & & \\ & 0 & 4 \cdot \sqrt{6 \cdot 2} \sqrt{\frac{2 \cdot 2}{5 \cdot 3}} & & \\ & & 0 & 4 \cdot \sqrt{7 \cdot 1} \sqrt{\frac{3 \cdot 3}{7 \cdot 5}} & \\ & & & 0 & \\ & & & & 0 \end{bmatrix} \quad (13)$$

The basis vectors are  $|N = 4, L, M = 0\rangle = |N = 4, \frac{L}{M}\rangle$ , ordered in  $L$  from smallest ( $L = 0$ ) to largest ( $L = 3$ ). This matrix is real and symmetric. Only the diagonal matrix elements (all 0) and the nonzero matrix elements above the main diagonal are shown.

The eigenvalues and eigenvectors are:

$$\begin{array}{c|cccc} \text{Energy} & |0\rangle & |1\rangle & |2\rangle & |3\rangle \\ \hline \Delta E & \begin{array}{c} 0 \\ 0 \end{array} & \begin{array}{c} 1 \\ 0 \end{array} & \begin{array}{c} 2 \\ 0 \end{array} & \begin{array}{c} 3 \\ 0 \end{array} \\ \hline 12 & \sqrt{5/20} & \sqrt{9/20} & \sqrt{5/20} & \sqrt{1/20} \\ 4 & -\sqrt{5/20} & -\sqrt{1/20} & \sqrt{5/20} & \sqrt{9/20} \\ -4 & -\sqrt{5/20} & \sqrt{1/20} & \sqrt{5/20} & -\sqrt{9/20} \\ -12 & -\sqrt{5/20} & \sqrt{9/20} & -\sqrt{5/20} & \sqrt{1/20} \end{array} \quad (14)$$

Eigenvalues are measured in units  $\Delta E = \frac{3}{2}|eE|a_0$ . Here  $|eE|a_0$  is an electric dipole energy.

For the 3 states with  $M = 1$  the perturbation matrix is:

$$M = \pm 1 \quad \frac{3}{2} \times |eE|a_0 \times \begin{bmatrix} 0 & 4 \cdot \sqrt{6 \cdot 2} \sqrt{\frac{3 \cdot 1}{5 \cdot 3}} & & \\ & 0 & 4 \cdot \sqrt{7 \cdot 1} \sqrt{\frac{4 \cdot 2}{7 \cdot 5}} & \\ & & & 0 \end{bmatrix} \quad (15)$$

The basis vectors are  $|N = 4, L, M = \pm 1\rangle$ , ordered in  $L$  from smallest ( $L = 1$ ) to largest ( $L = 3$ ). The eigenvalues and eigenvectors are:

$$\begin{array}{c|ccc}
\frac{\text{Energy}}{\Delta E} & \left| \begin{array}{c} 1 \\ \pm 1 \end{array} \right\rangle & \left| \begin{array}{c} 2 \\ \pm 1 \end{array} \right\rangle & \left| \begin{array}{c} 3 \\ \pm 1 \end{array} \right\rangle \\
\hline
8 & \sqrt{6/20} & \sqrt{10/20} & \sqrt{4/20} \\
0 & -\sqrt{8/20} & 0 & \sqrt{12/20} \\
-8 & \sqrt{6/20} & -\sqrt{10/20} & \sqrt{4/20}
\end{array} \quad (16)$$

The results remain the same for the matrix of states with  $M = -1$ .

For the 2 states with  $M = 2$  (as well as  $M = -2$ ) the perturbation matrix is:

$$M = \pm 2 \quad \frac{3}{2} \times |eE|a_0 \times \begin{bmatrix} 0 & 4 \cdot \sqrt{7 \cdot 1} \sqrt{\frac{5 \cdot 1}{7 \cdot 5}} \\ 0 & 0 \end{bmatrix} \quad (17)$$

The basis vectors are  $|N = 4, L, M = \pm 2\rangle$ , ordered in  $L$  from smallest ( $L = 2$ ) to largest ( $L = 3$ ). The eigenvalues and eigenvectors are:

$$\begin{array}{c|cc}
\frac{\text{Energy}}{\Delta E} & \left| \begin{array}{c} 2 \\ \pm 2 \end{array} \right\rangle & \left| \begin{array}{c} 3 \\ \pm 2 \end{array} \right\rangle \\
\hline
4 & 1/\sqrt{2} & 1/\sqrt{2} \\
-4 & -1/\sqrt{2} & 1/\sqrt{2}
\end{array} \quad (18)$$

The states  $|N = 4, L = 3, M = \pm 3\rangle$  are eigenstates of the perturbing hamiltonian with energy eigenvalue 0.

The spectrum of Stark energies is similar to the spectrum of Zeeman energies. Measured in units of  $N \times \frac{3}{2}|eE|a_0$ , the energies and their degeneracies are

$$\begin{array}{cccccccc}
\text{Energy}/(N \times \frac{3}{2}|eE|a_0) & -3 & -2 & -1 & 0 & +1 & +2 & +3 \\
\text{Degeneracy} & 1 & 2 & 3 & 4 & 3 & 2 & 1
\end{array} \quad (19)$$

This spectrum of energy eigenvalues is shown in Fig. 1

## 6 Arbitrary $N$

The nature of the Stark spectrum computed for  $N = 4$  persists for higher (and lower) values of  $N$ . However, the spacing between levels depends on  $N$ . It is simple to determine this  $N$ -dependence as follows. We construct and diagonalize the  $2 \times 2$  matrix for the states with arbitrary  $N$  and  $M = N - 2$ . This matrix mixes the states  $|N, L = N - 2, M = N - 2\rangle$  and  $|N, L = N - 1, M = N - 2\rangle$ .

The off-diagonal matrix element is  $-\frac{3}{2}|eE|a_0 \times N \sqrt{N^2 - (N - 1)^2} \times \sqrt{\frac{(2N-3)(1)}{(2N-1)(2N-3)}} = \frac{3}{2}N|eE|a_0$ . The eigenvalues of this  $2 \times 2$  matrix are  $\pm \frac{3}{2}N|eE|a_0$ . As a result, the spacing between adjacent Stark levels in the perturbed multiplet is  $\Delta E = \frac{3}{2}N|eE|a_0$  and the spectrum is  $k \times \Delta E$ , with  $k = 0, \pm 1, \pm 2, \dots, \pm(N - 1)$ . The degeneracy of the level with energy  $k\Delta E$  is  $N - |k|$ .

## 7 Stark States

Under the influence of an external electric field, the ‘‘good quantum numbers’’ for the states of the hydrogen atom are  $N$  and  $M$ , for the field mixes states with different  $L$  in the range  $|M| \leq L \leq N - 1$ .

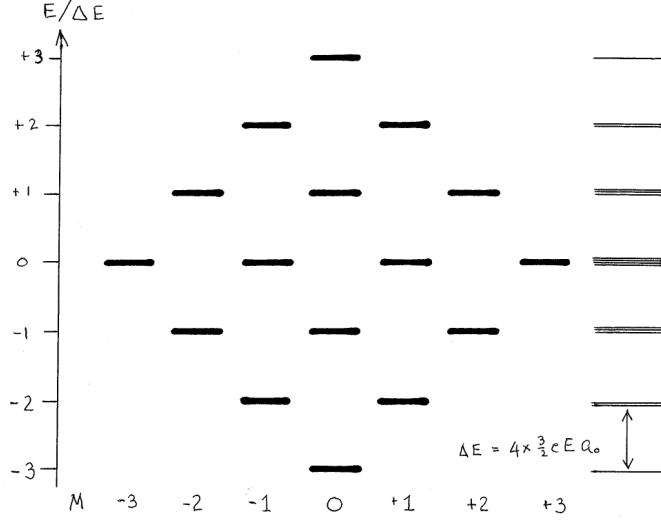


Figure 1: Energy eigenvalues of the Stark perturbation in the  $N = 4$  multiplet of atomic hydrogen. The energies are shown as a function of the magnetic quantum number  $M$  (horizontal). The orbital angular momentum  $L$  is no longer a good quantum number since rotational symmetry is broken by the perturbation  $\mathcal{H}_{pert} = -e\mathbf{E} \cdot \mathbf{r}$ . This perturbation mixes states with the same  $M$  and different  $L$ . Energy spacing is  $N \times \frac{3}{2}eEa_0$ .

It is useful to introduce an “internal quantum number”  $k$  to lift the  $N, M$  degeneracy. We define this index to range from a maximum  $k = N - 1 - |M|$  to the negative  $k = -(N - 1 - |M|)$  in *even* steps. As an example, the three states with  $N = 4, M = \pm 1$  are

$$[ |4, \pm 1, +2\rangle \quad |4, \pm 1, 0\rangle \quad |4, \pm 1, -2\rangle ] = [ |4, 1, \pm 1\rangle \quad |4, 2, \pm 1\rangle \quad |4, 3, \pm 1\rangle ] \begin{bmatrix} \sqrt{\frac{6}{20}} & -\sqrt{\frac{8}{20}} & \sqrt{\frac{6}{20}} \\ \sqrt{\frac{10}{20}} & 0 & -\sqrt{\frac{10}{20}} \\ \sqrt{\frac{4}{20}} & \sqrt{\frac{12}{20}} & \sqrt{\frac{4}{20}} \end{bmatrix} \quad (20)$$

The basis states on the left are Stark eigenstates  $|NMk\rangle$  with internal index  $k = +2, 0, -2$  while the basis states on the right are the better-known spherically symmetric eigenstates  $|NLM\rangle$  with internal quantum number  $M$ . The energies of stark eigenstate  $|NMk\rangle$  are

$$E(NMk) = E_N + \left( \frac{3}{2} |eE| a_0 N \right) \times k = E_N + \mu_E |E| N k \quad (21)$$

with  $E_N$  the energy of the unperturbed hydrogen state  $E_g/N^2$  and  $\mu_E = \frac{3}{2}|e|a_0$ .

## 8 Secular Equation

For any  $N$ , every matrix element is proportional to  $N$  through the radial integral given in Eq. (6). It is useful to remove this factor from the matrices  $\langle NLM| -e\mathcal{E}z|NL-1M\rangle$ , along with the factors  $-\frac{3}{2}e\mathcal{E}a_0$ . The resulting matrices still depend on  $N$  but the secular equation for these matrices depends only on the size of the matrices. The results for  $1 \times 1, 2 \times 2, 3 \times 3, \dots$  matrices are:

Matrix Size	Secular Equation	
$1 \times 1$	$-\lambda$	
$2 \times 2$	$(\lambda^2 - 1^2)$	
$3 \times 3$	$-\lambda(\lambda^2 - 2^2)$	(22)
$4 \times 4$	$(\lambda^2 - 1^2)(\lambda^2 - 3^2)$	
$5 \times 5$	$-\lambda(\lambda^2 - 2^2)(\lambda^2 - 4^2)$	
$\dots$	$\dots$	

The spectrum of eigenvalues reflects the symmetry of the Stark spectrum.

## 9 Transition Intensities

Transitions from states in a multiplet with principal quantum number  $N$  to states in the  $N'$  multiplet occur at closely bunched energies

$$E_N - E_{N'} + \mu_E |E| (Nk - N'k') \quad (23)$$

The transitions occur with different intensities. These intensities can be computed. We illustrate how this can be done for the relatively simple case  $N = 3$  and  $N' = 2$ .

For radiation emitted parallel to the direction of the external electric field ( $\mathbf{k} \parallel \mathbf{E}$ ), plane polarized radiation is emitted due to transitions with  $\Delta M = 0$  and circularly polarized radiation is emitted due to transitions with  $\Delta M = \pm 1$ . The amplitudes for plane polarized radiation are

$$\langle N'Mk'|z|NMk\rangle = \sum_{L'} \sum_L \langle N'Mk'|N'L'M\rangle \langle N'L'M|z|NLM\rangle \langle NLM|NMk\rangle \quad (24)$$

We have inserted a complete set of states (sums over  $L', L$ ) on the right hand side of the matrix element on the left. This is the matrix element that determines the amplitude of the linearly polarized transition.

In the case  $N = 3, M = 0$  the matrix on the right ( $\langle NLM|NMk\rangle$ ) has  $L = 0, 1, 2$  and  $k = +2, 0, -2$ . It is a  $3 \times 3$  matrix that transforms from the  $|NLM\rangle$  basis to the  $|NMk\rangle$  basis. The matrix elements are obtained by diagonalizing a  $3 \times 3$  matrix of the form given in Eq. (?). We find:

$$[ |3, 0, +2\rangle \quad |3, 0, 0\rangle \quad |3, 0, -2\rangle ] = [ |3, 0, 0\rangle \quad |3, 1, 0\rangle \quad |3, 2, 0\rangle ] \begin{bmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} \\ \sqrt{\frac{1}{2}} & 0 & \sqrt{\frac{1}{2}} \\ \sqrt{\frac{1}{6}} & -\sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{6}} \end{bmatrix} \quad (25)$$

Similarly, for the Stark states with  $M = 0$  in the  $N' = 2$  multiplet:

$$[ |2, 0, +1\rangle \quad |2, 0, -1\rangle ] = [ |2, 0, 0\rangle \quad |2, 1, 0\rangle ] \begin{bmatrix} \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}} \\ \sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} \end{bmatrix} \quad (26)$$

The matrix elements of the transition operator  $z$  between initial states in the  $N = 3$  multiplet and final states in the  $N' = 2$  multiplet are first computed in the spherical basis. For  $M = 0$  we have

$$\langle 2L'0|z|3L0\rangle = \int_0^\infty R_{2L'}(r)rR_{3L}(r)dr \times \sqrt{\frac{4\pi}{3}} \int d\Omega Y_0^{L'} Y_0^1 Y_0^L \quad (27)$$

The radial integrals can be computed analytically:

	$R_{30}$	$R_{31}$	$R_{32}$	
$R_{20}$	$\frac{11808\sqrt{6}}{15625}$	$\frac{27648\sqrt{3}}{15625}$	$-\frac{119808\sqrt{15}}{78125}$	(28)
$R_{21}$	$\frac{10368\sqrt{2}}{15625}$	$-\frac{27648}{15625}$	$\frac{165888\sqrt{5}}{78125}$	

In a similar format, the angular integrals are

	$L = 0$	$L = 1$	$L = 2$	
$L' = 0$	$0$	$\sqrt{1/3}$	$0$	(29)
$L' = 1$	$\sqrt{1/3}$	$0$	$\sqrt{4/15}$	

The values of  $\langle 2L'0|z|3L0\rangle$  are the element by element products of the previous two results. This  $2 \times 3$  matrix must be multiplied by a  $3 \times 3$  matrix on the right and a  $2 \times 2$  matrix on the left to construct the matrix elements of  $z$  in the Stark basis. The  $3 \times 3$  matrix is shown in Eq. (28) and the  $2 \times 2$  matrix is the inverse (transpose) of that shown in Eq. (29). Specifically, we have

$$\begin{aligned} \langle 2L'0|z|3L0\rangle &= \begin{bmatrix} \sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} \\ -\sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} \end{bmatrix} \begin{bmatrix} 0 & \frac{27648}{15625} & 0 \\ \frac{3456\sqrt{6}}{15625} & 0 & \frac{110592\sqrt{75}}{390625} \\ \frac{15625}{15625} & 0 & \frac{390625}{390625} \end{bmatrix} \begin{bmatrix} \sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} \\ \sqrt{\frac{1}{2}} & 0 & -\sqrt{\frac{1}{2}} \\ \sqrt{\frac{1}{6}} & \sqrt{\frac{2}{3}} & \sqrt{\frac{1}{6}} \end{bmatrix} \\ &= \begin{bmatrix} \frac{141696}{78125} & \frac{93312}{78125} & \frac{3456}{78125} \\ \frac{3456}{78125} & \frac{93312}{78125} & \frac{141696}{78125} \end{bmatrix} \end{aligned} \quad (30)$$

The transition intensities are the squares of these transition amplitudes:

$$|\langle 2, M = 0, k'|z|3, M = 0, k\rangle|^2 \quad \rightarrow \quad \begin{array}{c|ccc} & k = +2 & k = 0 & k = -2 \\ \hline k' = +1 & 1.813708 & 1.194393 & 0.044236 \\ k' = -1 & 0.044236 & 1.194393 & 1.813708 \end{array} \quad (31)$$

In addition to these transitions, linearly polarized radiation is emitted from transitions  $|3M, k\rangle \rightarrow |2Mk'\rangle$  with  $M = +1$  and  $M = -1$ . These amplitudes are

$$\begin{aligned} &\langle 2, M = 1, k' = 0|z|3, M = 1, k = \pm 1\rangle = \\ &\langle 2, M = 1, k' = 0|2, L' = 1, M = 1\rangle \langle 2, L' = 1, M = 1|z|3, L, M = 1\rangle \langle 3, L, M = 1|3, M = 1, k = \pm 1\rangle \end{aligned} \quad (32)$$



On the right hand side of this equation,  $\langle 2, M = 1, k' = 0 | 2, L' = 1, M = 1 \rangle = 1$ , the coefficients  $\langle 3, L, M = 1 | 3, M = 1, k = \pm 1 \rangle$  with  $L = 1, 2$  are  $\pm 1/\sqrt{2}$ , and the matrix element of  $z$  is  $(\int R_{21}rR_{32}dr) \sqrt{\frac{(2+1)(2-1)}{(2\cdot 2+1)(2\cdot 2-1)}} = \frac{165888\sqrt{5}}{78125} \times \sqrt{\frac{3\cdot 1}{5\cdot 3}}$ . The probabilities of these two transitions are equal to each other and are 2.123366. Since these two transitions ( $M = +1$  and  $M = -1$ ) have the same energy, the total relative intensity observed at this energy is the sum of the two separate intensities: 4.246732.

## 10 Overlap of Multiplets

The diagonalizations above have been carried out assuming that adjacent principal quantum number multiplets are sufficiently isolated so that matrix elements between states with  $N$  and  $N \pm 1$  are unimportant. Multiplets  $N$  and  $N + 1$  begin mixing when the highest energy of multiplet  $N$ ,  $E_N + (N - 1)N(\frac{3}{2}eEa_0)$ , is approximately equal to the lowest energy of the next higher multiplet,  $E_{N+1} - N(N + 1)(\frac{3}{2}eEa_0)$ . The mixing condition is

$$-\frac{mc^2\alpha^2}{2N^2} + (N - 1) \times \frac{3}{2}eEa_0N \simeq -\frac{mc^2\alpha^2}{2(N + 1)^2} - (N + 1 - 1) \times \frac{3}{2}eEa_0(N + 1) \quad (33)$$

For fixed electric field  $E$  the eigenstates begin to overlap when

$$\frac{2N + 1}{(2N^2)N^2(N + 1)^2} = \frac{\frac{3}{2}eEa_0}{\frac{1}{2}mc^2\alpha^2} \quad (34)$$

For small electric field  $E$ , the value of  $N$  at which overlap occurs is

$$N_{\text{O.L.}} \simeq \left( \frac{1}{2}mc^2\alpha^2 / \frac{3}{2}eEa_0 \right)^{1/5} \quad (35)$$

For example, in an external electric field of strength 100,000 V/cm [1],  $N_{\text{O.L.}} \simeq (13.6 / (1.5 * 10^5 * 0.5 * 10^{-8}))^{1/5} \simeq 7.1$ .

## 11 Sparking

The Coulomb potential, in the presence of a constant static electric field  $\mathbf{E}$ , is nonbinding. The total potential  $V_{\text{Tot}} = -\frac{e^2}{r} - eEz$  is shown along the  $z$  axis in Fig. 2. This potential has a local maximum at  $z = \sqrt{e^2/(eE)}$  whose value is  $V_{cb} = -2\sqrt{(e^2/a_0) * (eEa_0)}$  ( $cb = \text{Coulomb barrier}$ ). No bound state is stable. States with  $Re(E) > V_{cb}$  are not localized. They are extracted from the hydrogen atom by a process akin to sparking. States with  $Re(E) < V_{cb}$  will be confined to the region around the proton ( $|z| < \sqrt{e^2/(eE)}$ ) for a time determined by the imaginary part of the energy,  $Im(E)$ . The escape time behaves as  $\sim e^{-\hbar/Im(E)}$ . Except for states with energies very close to  $V_{cb}$ , the localized states will remain bound long enough for experimental purposes. The complex energies associated with the non squareintegrable wavefunctions can be computed using the powerful techniques of complex scaling that are beyond the scope of this discussion.

The Coulomb barrier height  $V_{cb}$  corresponds to a principal quantum number  $N$  determined by

$$-\frac{1}{2}mc^2\alpha^2 \frac{1}{N_{\text{sp}}^2} = -2\sqrt{\frac{e^2}{a_0} \times eEa_0} \quad (36)$$

Since  $e^2/a_0 = mc^2\alpha^2$ , for  $E = 10^5$  V/cm.

$$N_{\text{sp}} = \left(\frac{3}{16}\right)^{1/4} \left(\frac{\frac{1}{2}mc^2\alpha^2}{\frac{3}{2}eEa_0}\right)^{1/4} = 7.6 \quad (37)$$

In short, the atom will be pulled apart the by external electric field at values of  $N$  about the same as those at which the adjacent principal quantum levels begin to overlap.

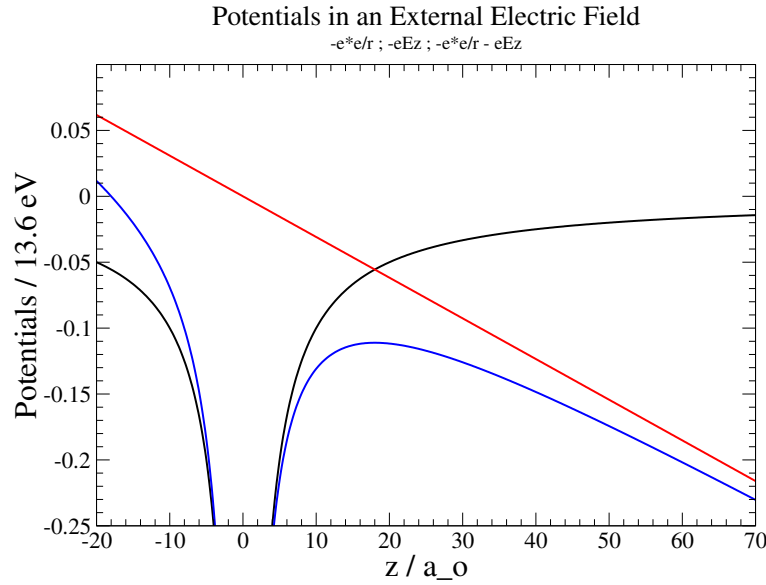


Figure 2: The total potential is the sum of the Coulomb potential,  $-e^2/r$ , and the potential due to the external electric field,  $-eEz$ . This potential has a maximum that extends to  $+\infty$  and a minimum that extends to  $-\infty$ . It is therefore not a binding potential: all states that are localized near the proton (at the origin) eventually leak away to  $z \rightarrow \infty$ . The decay time is exponentially large, and can be neglected for all practical purposes except for states with  $E$  very close to  $V_{cb}$ .

## 12 $N = 1$

For the ground state  $|NLM\rangle = |100\rangle$ , there is no degeneracy, neglecting electron and nuclear spin. As a result, perturbation theory for nondegenerate states can be applied. In first order there is no effect. In second order we find

$$\Delta E_{100} = - \sum_{\text{ex.st.}} \frac{|\langle NLM | (-eEz) | 100 \rangle|^2}{E_{NLM} - E_{100}} \quad (38)$$

The sum extends over “all” excited states, the nonzero matrix elements are those with  $M = 0$  and  $L = 1$ , for which we have

$$|\langle NLM | -eEz | 100 \rangle|^2 = (eEa_0)^2 \times \frac{2^8 N^7 (N-1)^{2N-5}}{3(N+1)^{2N+5}} \quad (39)$$

The denominator in Eq.(18) is the energy difference  $E_N - E_1 = -\frac{1}{2}mc^2\alpha^2(\frac{1}{N^2} - \frac{1}{1^2})$ . Here  $mc^2$  is the electron rest energy,  $\alpha = \frac{e^2}{\hbar c}$  is the fine structure constant, and  $-\frac{1}{2}mc^2\alpha^2$  is the ground state energy of the hydrogen atom. With these results, we find numerically

$$\Delta E_{100} = -\frac{(eEa_0)^2}{\frac{1}{2}mc^2\alpha^2} \times \sum_{N=2}^{\infty} \frac{N^2}{N^2-1} \times \frac{2^8 N^7 (N-1)^{2N-5}}{3(N+1)^{2N+5}} \xrightarrow{\text{Maple}} -2E^2 a_0^3 \times 0.9158144726... \quad (40)$$

The polarizability,  $\alpha_p$ , of the hydrogen atom is related to its ground state energy change in an electric field by  $\Delta E_{100} = -\frac{1}{2}\alpha_p E^2$ . Comparing this definition of the classical polarizability with the quantum mechanical result in second order perturbation theory, we find  $\alpha_p = 3.663257890 a_0^3$ .

This perturbation result is a little too small, for two reasons:

1. We have not carried out the perturbation calculation beyond second order.
2. The bound states over which the summation takes place do not constitute a complete set of states. "All" the states include scattering ( $E > 0$ ) states with  $L = 1$  as well as the bound states with  $L = 1$ .

**Remark:** Neglecting a subset of the complete set of states has two effects. First, the perturbed energies cannot be estimated correctly. Second, it is not possible to localize a particle to a delta function: the minimum diameter in configuration space is determined by the subset of neglected states. This problem occurs in the Dirac theory of the electron. Neglecting the "negative energy" states predicted by the Dirac equation is responsible, in the same way, for our inability to localize any state in configuration space of the Dirac equation to less than about a Compton wavelength:  $\lambda_C = \frac{\hbar}{mc}$ .

## 13 Variational Bound

The polarization can also be estimated by searching for a good upper bound on the ground state energy in the presence of an external electric field. In order to do this, we return to the original formulation of wave mechanics by Schrödinger in his very first paper on the subject [3]. The original formulation (c.f., Eq.(3) in [3]) was as a variational principle, where the action

$$A = \int \left( \frac{\hbar^2}{2m} \nabla\psi \cdot \nabla\psi + V\psi^2 \right) dV \quad (41)$$

is to be minimized subject to the condition that the norm of the wavefunction is fixed:  $\int \psi^2 dV = 1$ .

In order to carry out such a computation, we perturb off the known  $1S$  ground state with a term that respects the symmetry of the perturbation. The perturbation is expressed in terms of parameters that must be varied to locate a minimum. We choose the following parameterized approximation to the wavefunction:

$$\psi_{100}(r, \theta, \phi) \rightarrow \left( \frac{1}{a_0} \right)^{3/2} (2+p(r) \cos(\theta)) e^{-r/a_0} \quad p(r) = a_0 + a_1(r/a_0) + a_2(r/a_0)^2 + a_3(r/a_0)^3 \quad (42)$$

Before substituting this parameterized wavefunction into the variational expression we first extract the dimensional quantities to convert the integral to dimensionless form. This is done by the substitution  $r = a_0 y$ , where  $a_0 = \hbar^2/mc^2$  is the Bohr radius. Under this substitution the action integral becomes

$$A = \int \int \frac{e^2}{2a_0} \nabla \psi \cdot \nabla \psi - \frac{e^2}{a_0} \frac{1}{y} \psi^2 + e\mathcal{E}a_0 \psi^2 (y \cos(\theta)) y^2 dy \sin \theta d\theta \quad (43)$$

In obtaining this expression the factors  $1/a_0^3$  that come from  $\psi(r)^2$  are combined with the volume element  $r^2 dr$  to obtain  $y^2 dy$ .  $E = \hbar^2/2ma_0^2 = 13.6$  eV The electron binding energy is  $-e^2/2a_0 = -13.6$  eV, which sets the scale for this calculation. Cleaning up gives

$$A/\left(\frac{e^2}{2a_0}\right) = \int \int \nabla \psi \cdot \nabla \psi - 2\frac{1}{y} \psi^2 + \gamma \psi^2 (y \cos(\theta)) y^2 dy \sin \theta d\theta \quad (44)$$

where  $\gamma = e\mathcal{E}a_0/E$  is the ratio of the electric dipole energy to the binding energy in the hydrogen ground state. This dimensionless ratio is typically small. For future convenience we note that  $\gamma^2/(e^2/2a_0) = 2a_0^3\mathcal{E}^2$ .

After these simplifications the parameterized wavefunction can be substituted into this expression. Before doing so we step back for a few simplifying considerations. The integrals involve the square of the parameterized wavefunction; the wavefunction is linear in the parameters; therefore the result can contain terms only up to order 2 in the unknown parameters. By symmetry, the kinetic energy integral, the integral involving the Coulomb energy, and the overlap integral are *even* in the parameters. By symmetry also, the integral involving  $e\mathcal{E}z$  is odd, so involves only linear terms in the coefficients. The first three integrals can be expressed as a constant plus a quadratic form in the  $a_i$  while the linear terms can be expressed in the form  $t_i a_i$ . Using the expression

$$\nabla = \hat{y} \frac{\partial}{\partial y} + \hat{\theta} \frac{1}{y} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{y \sin \theta} \frac{\partial}{\partial \phi} \quad (45)$$

and  $dV = y^2 dy \sin(\theta) \theta d\phi$ , Maple was requested to carry out the four integrals, with the following results:

$$\begin{aligned} \int \nabla \psi \cdot \nabla \psi dV &= 2 + \frac{1}{2} MKE_{ij} a_i a_j \\ \int \psi^2 / y dV &= 2 + \frac{1}{2} MPE_{ij} a_i a_j \\ \int \psi^2 dV &= 2 + \frac{1}{2} MOL_{ij} a_i a_j \\ \int \psi^2 y dV &= t_i a_i \end{aligned} \quad (46)$$

The matrices involved in the kinetic energy integral, the Coulomb potential energy integral, and the overlap integral, and the vector involved in the Stark perturbation integral are

$$\begin{aligned} MKE &= \begin{bmatrix} \frac{5}{3} & \frac{5}{6} & \frac{2}{3} & \frac{1}{2} \\ \frac{5}{6} & 1 & \frac{2}{3} & \frac{2}{3} \\ \frac{2}{3} & \frac{2}{3} & \frac{7}{2} & \frac{35}{4} \\ \frac{1}{2} & \frac{2}{3} & \frac{35}{4} & 30 \end{bmatrix} & PKE &= \begin{bmatrix} \frac{1}{3} & \frac{1}{3} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{3} & \frac{1}{2} & \frac{1}{2} & \frac{5}{2} \\ \frac{1}{2} & \frac{1}{2} & \frac{5}{2} & \frac{15}{2} \\ 1 & \frac{5}{2} & \frac{15}{2} & \frac{105}{4} \end{bmatrix} \\ MOL &= \begin{bmatrix} \frac{1}{3} & \frac{1}{2} & 1 & \frac{5}{2} \\ \frac{1}{2} & 1 & \frac{5}{2} & \frac{15}{2} \\ 1 & \frac{5}{2} & \frac{15}{2} & \frac{105}{4} \\ \frac{5}{2} & \frac{15}{2} & \frac{105}{4} & 105 \end{bmatrix} & t &= \begin{bmatrix} 1 \\ 2 \\ 5 \\ 15 \end{bmatrix} \end{aligned} \quad (47)$$

The perturbed energy is determined by finding the stationary value of the Action Integral. There are two equivalent ways to determine this minimum. The brute force way is to construct the ratio  $\langle \psi | H_0 + H_{Pert} | \psi \rangle / \langle \psi | \psi \rangle$ . The numerator in this expression contains a constant term and terms that are linear and quadratic in the unknown amplitudes  $a_i$ . The expression to be minimized is

$$\frac{E}{e^2/2a_0} = \frac{(2 + \frac{1}{2}MKE_{ij}a_ia_j) - 2(2 + \frac{1}{2}MPE_{ij}a_ia_j) + \gamma t_ia_i}{2 + \frac{1}{2}MOL_{ij}a_ia_j} \quad (48)$$

When this is cleaned up and expanded to second order in the coefficients  $a$  we find

$$-1 + \frac{1}{2}(MKE - 2MPE + OL)_{ij} a_ia_j + \gamma t_ia_i \quad (49)$$

to be minimized. Standard procedures lead to

$$a_i = -\gamma(MKE - 2MPE + MOL)^{-1}t_i \quad (50)$$

The matrix product  $t_i ((MKE - 2MPE + MOL)^{-1})_{ij} t_j = \frac{9}{2}$ . When this solution is substituted into Equation (XX) we find

$$E(\mathcal{E}) = -\frac{e^2}{2a_0} - \frac{9}{4}a_0^3\mathcal{E}^2 \quad (51)$$

By comparing this with the classical expression for the energy stored in a medium with a linear polarizability  $\alpha$ , which is  $-\frac{1}{2}\alpha\mathcal{E}^2$ , we find

$$\alpha = \frac{9}{2}a_0^3 \quad (52)$$

## 14 Conclusion

We have exploited symmetry to reduce the computational complexity of the Stark perturbation problem. We choose as an unperturbed set of basis vectors the hydrogen bound states  $|N \frac{L}{M}\rangle = \psi_{NLM}(r, \theta, \phi) = \frac{1}{r}R_{N,L}(r)Y_M^L(\theta, \phi)$ . We also choose our  $z$  axis in the direction of the external electric field  $\mathbf{E}$ . We apply symmetry arguments to the matrix elements

$$\langle N'L'M'|\mathcal{H}_{pert}|NLM\rangle$$

Since  $\mathbf{r}$  is a vector operator (Rank 1 tensor operator), all matrix elements vanish unless  $\Delta L = \pm 1, 0$ , by the Wigner-Eckart theorem. Since  $\mathbf{r}$  has odd parity, the matrix elements with  $L' = L$  or  $\Delta L = 0$  vanish. By  $SO(2)$  rotational symmetry the matrix elements with  $M' \neq M$  all vanish. By reflection symmetry in a plane containing the  $z$  axis, matrix elements with  $M$  are equal to those with  $-M$ . Finally, we make an approximation that the mixing between principal quantum levels can be neglected compared to the intra-level matrix elements:  $\Delta N = 0$ . The three symmetries and one approximation yield the simplification:

$$\langle N'L'M'|\mathcal{H}_{pert}|NLM\rangle = \delta_{N'N}\delta_{M'M}\delta_{L',L\pm 1} eEa_0 \mathcal{R}(N, L' \leftrightarrow L) \mathcal{A}(L' \leftrightarrow L, M)$$

Simple explicit expressions exist for the two factors on the right. The  $N^2 \times N^2$  perturbation matrix for the  $N$ th principal quantum level can be written as the direct sum of smaller matrices: one  $N \times N$  and two  $k \times k$  matrices, with  $k = 1, 2, \dots, N - 1$ . The two  $k \times k$  matrices are identical, courtesy of planar reflection symmetry. For each  $k \times k$  matrix only  $k - 1$  different matrix elements need be computed. Each nonzero matrix element is the product of two factors: a radial factor and an angular factor. The matrices can be diagonalized separately. The energy eigenvalues have the form  $k \times \Delta E$ , where  $\Delta E = N \times \frac{3}{2}eEa_0$ . The spectrum has the regular form shown in Fig. 1.

This simple treatment breaks down as  $N$  increases. It can break down in two ways:

1. The perturbed states in two adjacent principal quantum levels can begin to overlap.
2. The energies of the states in level  $N$  are higher than the Coulomb barrier height. They are therefore unbound.

Finally, we employed two different methods to estimate the electric dipole moment of the hydrogen atom in its ground state. The first method was a direct application of second order perturbation theory, including a sum over the nonzero matrix elements of the electric dipole operator between the ground states and all bound excited states  $|NLM\rangle$  with  $N > 1, L = 1, M = 0$ . These matrix elements are known and the sum was carried out numerically. This sum excluded the scattering states, and so lead to a result  $\alpha \simeq 3.6$  smaller than a better estimate.

The better estimate was obtained by introducing a parameterized representation of the ground state wavefunction into the Action Integral formulation of wave mechanics originally proposed by Schrödinger. It is possible to compute all the integrals in this action integral. The integrals give constants and terms that are linear and bilinear in the unknown parameters. These parameters are determined by standard methods and, when substituted back into the action integral, give the ground state energy correction to second order in the external applied electric field  $\mathcal{E}$ . From this expression we constructed a value for the electric polarizability  $\alpha$ .

## 15 Appendix

Many variational estimates take the form

$$\frac{\langle \psi(a) | H_{\text{pert}} | \psi(a) \rangle}{\langle \psi(a) | \psi(a) \rangle} \rightarrow \frac{t_i a_i}{1 + \frac{1}{2} Q_{ij} a_i a_j} \quad (53)$$

Here it is assumed that the wave function is approximated as a linear combination of terms of known form, for example as shown in Sec. 13. The matrix  $Q$  is positive definite.

The values of the parameters  $a$  that minimize this estimate, and the minimum value, are obtained as follows. The constraint is enforced using Lagrange multipliers:

$$\frac{\partial}{\partial a_i} (\langle \psi(a) | H_{\text{pert}} | \psi(a) \rangle - \lambda \langle \psi(a) | \psi(a) \rangle) \rightarrow t_i - \lambda Q_{ij} a_j = 0 \quad (54)$$

From this we see that all the unknown coefficients  $a_i$  have the same behavior:  $a_i = \lambda^{-1} Q_{ij}^{-1} t_j = s Q^{-1} t$ . This ansatz is placed into the ratio to give an estimate for the energy depending on a single variable  $s = \lambda^{-1}$ :

$$E(s) = \frac{st^t Q^{-1} t}{1 + \frac{s^2}{2} t^t Q^{-1} t} \quad (55)$$

The minimum occurs for  $s = -\sqrt{2/t^t Q^{-1} t}$ , so that the variables are  $a_i = -\sqrt{2/(t^t Q^{-1} t)} Q_{ij}^{-1} t_j$  and the minimum value is  $E_{\text{min}} = -\sqrt{\frac{1}{2} t^t Q^{-1} t}$ .

## References

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