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, 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 $k = 0, 1, 2, \cdots, N-1$. The splitting is indicated in Fig. 1.

The perturbing hamiltonian is introduced in Sect. 2. In Sect. 3 we construct the matrix elements of this hamiltonian. The effects of symmetry on this computation are described in Sect. 4 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. 7 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. I n Sects. 8 and 9 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

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

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:

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

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

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

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 $-e\mathbf{E}\cdot\mathbf{r} = -e|\mathbf{E}|z$. Next, we replace $|\mathbf{E}| \to E$ and $z = r\cos(\theta) = \sqrt{\frac{4\pi}{3}}rY_0^1(\theta,\phi)$. The matrix elements to be computed are

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

The angular integral provides useful selection rules. First, $\Delta L = \pm 1, 0$. By parity arguments, the integral with $\Delta L = 0$ is zero. The only relevant integral is therefore

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

with $1 \leq L \leq N-1$. It is useful to observe that the integrals are unchanged under $M \to -M$.

The radial integral is

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

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

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

$$
\begin{bmatrix}
 & * & & * & \\
 & & * & & * \\
* & & & * & \\
 & & & & * \\
 & * & & & \\
* & & * & & \\
 & & * & &
\end{bmatrix}
\qquad
\begin{array}{cc}
0 & 0 \\
1 & +1 \\
1 & 0 \\
1 & -1 \\
\hline
2 & +2 \\
2 & +1 \\
2 & 0 \\
2 & -1 \\
2 & -1
\end{array}
\tag{7}
$$

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:

$$
\begin{bmatrix}
 & & & & & \\
 & * & & & & \\
 & * & & & & \\
 & & & * & & \\
 & & * & & * & \\
 & & & * & & \\
 & & & & & * \\
 & & & & * & \\
 & & & & &
\end{bmatrix}
\qquad
\begin{array}{cc}
2 & +2 \\
1 & +1 \\
2 & +1 \\
\hline
0 & 0 \\
1 & 0 \\
2 & 0 \\
\hline
1 & -1 \\
2 & -1 \\
2 & -2
\end{array}
\tag{8}
$$

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 $\mid\genfrac{}{}{0pt}{}{L}{M}\rangle, L = |M|, |M|+1, \cdots, N-1$. 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 diagonalize one 3×3 and one 2×2 matrix to compute all eigenvalues and eigenstates. The 1×1 matrices are already diagonal. There is a total of 3 different matrix elements to compute.

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)

$$
\begin{array}{cccc}
 & L = & 3 & 2 & 1 \\
\mathcal{R}(4, L) = \tfrac{1}{a_0}\int_0^\infty R_{4,L}(r)\, r\, R_{4,L-1}(r)\,dr = & & \dfrac{3}{2}\cdot 4 \cdot \sqrt{7} & \dfrac{3}{2}\cdot 4 \cdot \sqrt{3\cdot 4} & \dfrac{3}{2}\cdot 4 \cdot \sqrt{3\cdot 5}
\end{array}
\tag{9}
$$

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

$$\mathcal{A}(L,M) = \sqrt{\frac{(L+M)(L-M)}{2L+1)(2L-1)}}$$

$$
\begin{array}{c}
& & & M \\
& & \pm 2 & \pm 1 & 0 \\
& 3 & \sqrt{\dfrac{5\cdot 1}{7\cdot 5}} & \sqrt{\dfrac{4\cdot 2}{7\cdot 5}} & \sqrt{\dfrac{3\cdot 3}{7\cdot 5}} \\
L & 2 & & \sqrt{\dfrac{3\cdot 1}{5\cdot 3}} & \sqrt{\dfrac{2\cdot 2}{5\cdot 3}} \\
& 1 & & & \sqrt{\dfrac{1\cdot 1}{3\cdot 1}}
\end{array}
\qquad (10)
$$

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 4×4, 3×3 and 2×2 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:

$$
M=0 \qquad \frac{3}{2}\times eEa_0 \times
\begin{bmatrix}
0 & 4\cdot\sqrt{5\cdot 3}\sqrt{\frac{1\cdot 1}{3\cdot 1}} & & \\
& 0 & 4\cdot\sqrt{4\cdot 3}\sqrt{\frac{2\cdot 2}{5\cdot 3}} & \\
& & 0 & 4\cdot\sqrt{7}\sqrt{\frac{3\cdot 3}{7\cdot 5}} \\
& & & 0
\end{bmatrix}
\qquad (11)
$$

The basis vectors are $|N=4, L, M=0\rangle = |N=4,\ {}^{L}_{M}\ \rangle$, 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:

Energy $\dfrac{}{\Delta E}$	$\left|{}^{0}_{0}\right\rangle$	$\left|{}^{1}_{0}\right\rangle$	$\left|{}^{2}_{0}\right\rangle$	$\left|{}^{3}_{0}\right\rangle$
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	$-\sqrt{5/20}$	$\sqrt{9/20}$	$-\sqrt{5/20}$	$\sqrt{1/20}$

$$(12)$$

Eigenvalues are measured in units $\Delta E = \frac{3}{2}eEa_0$. Here eEa_0 is an electric dipole energy.

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

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

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:

Energy $\dfrac{}{\Delta E}$	$\left|{}^{1}_{\pm 1}\right\rangle$	$\left|{}^{2}_{\pm 1}\right\rangle$	$\left|{}^{3}_{\pm 1}\right\rangle$
8	$\sqrt{6/20}$	$\sqrt{10/20}$	$\sqrt{4/20}$
0	$-\sqrt{8/20}$	0	$\sqrt{12/20}$
-8	$\sqrt{6/20}$	$-\sqrt{10/20}$	$\sqrt{4/20}$

$$(14)$$

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:

$$M = \pm 2 \qquad\qquad \frac{3}{2} \times eEa_0 \times \begin{bmatrix} 0 & 4 \cdot \sqrt{7}\sqrt{\frac{5 \cdot 1}{7 \cdot 5}} \\ & 0 \end{bmatrix} \tag{15}$$

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:

$$
\begin{array}{c|c|c}
\text{Energy} & \left|\begin{matrix}2\\\pm 2\end{matrix}\right\rangle & \left|\begin{matrix}3\\\pm 2\end{matrix}\right\rangle \\
\Delta E & & \\
\hline
4 & 1/\sqrt{2} & 1/\sqrt{2} \\
-4 & -1/\sqrt{2} & 1/\sqrt{2}
\end{array}
\tag{16}
$$

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 $N \times \frac{3}{2}eEa_0$, the energies and their degeneracies are

$$
\begin{array}{lccccccc}
\text{Energy}/(N \times \frac{3}{2}eEa_0) & -3 & -2 & -1 & 0 & +1 & +2 & +3 \\
\text{Degeneracy} & 1 & 2 & 3 & 4 & 3 & 2 & 1
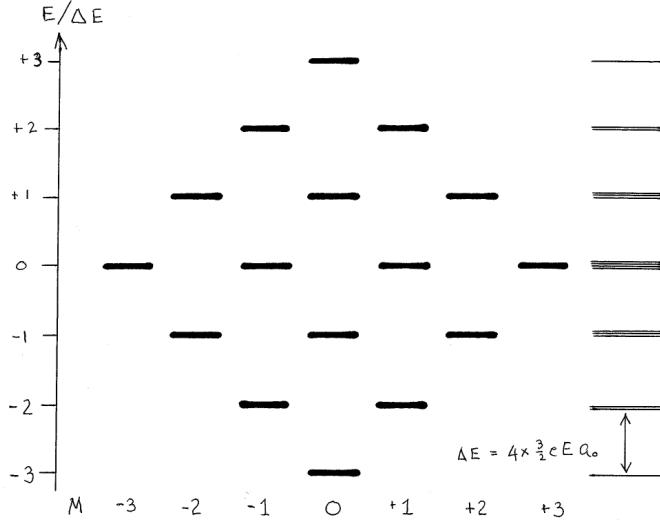\end{array}
\tag{17}
$$

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 $N \times \frac{3}{2}eEa_0$.

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 2×2 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 matrix element is $-\frac{3}{2}eEa_0 \times N\sqrt{N^2 - (N-1)^2} \times \sqrt{\frac{(2N-3)(1)}{(2N-1)(2N-3)}} = \frac{3}{2}NeEa_0$. The eigenvalues of this 2×2 matrix are $\pm\frac{3}{2}NeEa_0$. As a result, the spacing between adjacent Stark levels in the perturbed multiplet is $\Delta E = \frac{3}{2}NeEa_0$ and the spectrum is $k \times \Delta E$, with $k = 0, \pm 1, \pm 2, \cdots, \pm(N-1)$. The degeneracy of the level with energy $k\Delta E$ is $N - |k|$.

7 $N = 1$

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

$$\Delta E_{100} = -\sum_{\text{ex.st.}} -\frac{|\langle NLM|(-eEz)|100\rangle|^2}{E_{NLM} - E_{100}} \tag{18}$$

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

$$|\langle NLM| - eEz|100\rangle|^2 = (eEa_0)^2 \times \frac{2^8 N^7 (N-1)^{2N-5}}{3(N+1)^{2N+5}} \tag{19}$$

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

$$\Delta E_{100} = -\frac{(eEa_0)^2}{\frac{1}{2}mc^2\alpha^2} \times \sum_{N=2}^{\infty} \frac{N^2}{N^2 - 1} \times \frac{2^8 N^7 (N-1)^{2N-5}}{3(N+1)^{2N+5}} \xrightarrow{\text{Maple}} -2E^2 a_0^3 \times 0.9158144726... \tag{20}$$

The polarizability, α_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 $\alpha_p = 3.663257890\, a_0^3$. The polarizability can be computed by exactly solving for the ground state in the presence of the external electric field [2]. It is $\alpha_p = \frac{9}{2}\, a_0^3$.

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 uncertainty 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 Comptom wavelength: $\lambda_C = \frac{\hbar}{mc}$.

8   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

$$-\frac{mc^2\alpha^2}{2N^2} + (N-1)\times\frac{3}{2}eEa_0N \simeq -\frac{mc^2\alpha^2}{2(N+1)^2} - (N+1-1)\times\frac{3}{2}eEa_0(N+1) \qquad (21)$$

For fixed electric field E the eigenstates begin to overlap when

$$\frac{2N+1}{(2N)N^2(N+1)^2} = \frac{\frac{3}{2}eEa_0}{\frac{1}{2}mc^2\alpha^2} \qquad (22)$$

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

$$N_{\text{O.L.}} \simeq \left(\frac{1}{2}mc^2\alpha^2 / \frac{3}{2}eEa_0\right)^{1/4} \qquad (23)$$

For example, in an external electric field of strength $100,000$ V/cm [1], $N_{\text{O.L.}} \simeq (13.6/(1.5*10^5* 0.5*10^{-8})^{1/4} \simeq 6.5$.

9   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 = 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 manuscript.

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

$$-\frac{1}{2}mc^2\alpha^2\frac{1}{N_{\text{sp}}^2} = -2\sqrt{\frac{e^2}{a_0}\times eEa_0} \qquad (24)$$

Since $e^2/a_0 = mc^2\alpha^2$,

$$N_{\text{sp}} = \left(\frac{3}{64}\right)^{1/4}\left(\frac{\frac{1}{2}mc^2\alpha^2}{\frac{3}{2}eEa_0}\right)^{1/4} = 0.47*N_{O.L.} \qquad (25)$$

In short, the atom will be pulled apart the by external electric field at values of N smaller than those at which the adiacent principal quantum levels begin to overlap.
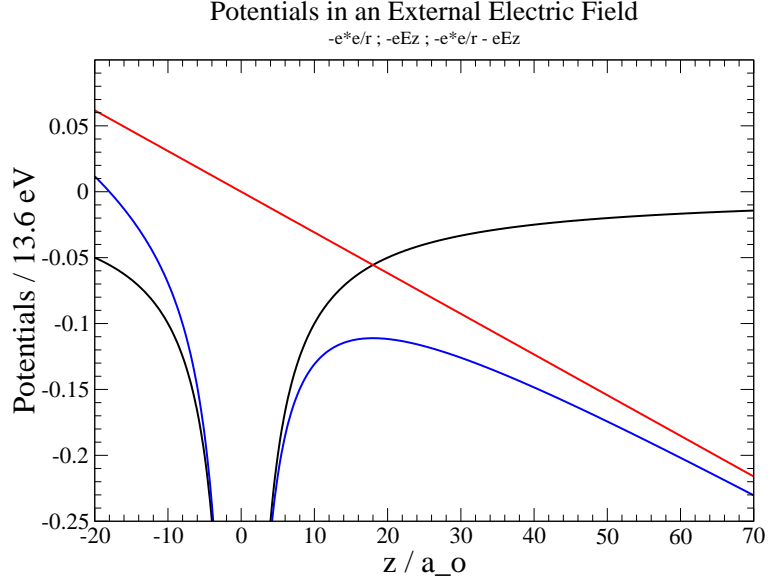

Figure 2: The total potential is the sum of the Coulomb potential, $-e^2/r$, and the potential due to the external electric field, $-eEz$. This potential has a maximum that extends to $+\infty$ and a minimum that extends to $-\infty$. It is therefore not a binding potential: all states that are localized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

10   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 $|N \begin{smallmatrix} L \\ M \end{smallmatrix} \rangle = \psi_{NLM}(r, \theta, \phi) = \frac{1}{r} R_{N,L}(r) Y_M^L(\theta, \phi)$. 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:

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

Simple explicit expressions exist for the two factors on the right. The $N^2 \times N^2$ perturbation matrix for the Nth principal quantum level can be written as the direct sum of smaller matrices: one $N \times N$ and two $k \times k$ matrices, with $k = 1, 2, \cdots, N-1$. 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.

We have seen the "sparking" occurs before overlap of adjacent principal qunatum levels takes place.

References

[1] J. Stark, Ann. d. Physik **48**, 193 (1915).

[2] E. Schrödinger, Quantization as an Eigenvalue Problem III. Ann. d. Physik (4)**80**, 437 (1926).