Excited State Stark Effect.

Lets now consider what happens to the *n=2* level (2s and 2p) in a constant electric field. It differs from the above 1s discussion because of the degeneracy of these states. Standard degenerate perturbation theory tells us that the first order shifts in the energy of the degenerate states are given by diagonalizing the matrix of the perturbation in the space of the degenerate functions. These functions are ψ_{200}, ψ_{210}, ψ_{211}, & ψ_{21-1} and the general matrix element is $\langle \psi_{2lm} | qrF\cos\theta | \psi_{2l'm'} \rangle$ or $\langle \psi_{2lm} | qFz | \psi_{2l'm'} \rangle$ and by parity all diagonal matrix elements are zero. Additionally, because the perturbation doesn't depend on ϕ a matrix element is zero unless the functions involved have the same magnetic quantum number. Consequently the only surviving matrix element is $\langle \psi_{200} | qrF\cos\theta | \psi_{210} \rangle = -3qF$. The matrix of the perturbation in this space is

$-3qF\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ with the eigenvalues $\pm 3qF$.

The linear combination of the degenerate functions corresponding to these eigenvalues are $\frac{1}{\sqrt{2}}(\psi_{200} - \psi_{210})$ & $\frac{1}{\sqrt{2}}(\psi_{200} + \psi_{210})$ for $3qF$ & $-3qF$ respectively and the first order effect of the electric field is to remove the degeneracy of ψ_{200} & ψ_{210} by forming sp hybrids polarized along with and opposite to the field