TlF ground state spectrum

Using the Hamiltonian from Table 1 of D.A. Wilkening, N.F. Ramsey, and D.J. Larson, Phys Rev A **29**, 425 (1984) (https://journals.aps.org/pra/abstract/10.1103/PhysRevA.29.425).

TABLE I. TlF hyperfine Hamiltonian.

$$\mathcal{H}_{\text{hyperfine}} = \mathcal{H}_{\text{rot}} + \mathcal{H}_S + \mathcal{H}_Z + \mathcal{H}_{sr} + \mathcal{H}_{ss}$$

where

$$\mathcal{H}_{\text{rot}} = hB\vec{J}^2$$

$$\mathcal{H}_S = -\vec{\mu}_e \cdot \vec{E}$$

$$\mathcal{H}_Z = -\frac{\mu_J}{J}(\vec{J}\cdot\vec{B}) - \frac{\mu_1}{I_1}(\vec{I}_1\cdot\vec{B}) - \frac{\mu_2}{I_2}(\vec{I}_2\cdot\vec{B})$$

$$\mathcal{H}_{sr} = c_1(\vec{I}_1\cdot\vec{J}) + c_2(\vec{I}_2\cdot\vec{J})$$

$$\mathcal{H}_{ss} = 5c_3\left[\frac{3(\vec{I}_1\cdot\vec{J})(\vec{I}_2\cdot\vec{J}) + 3(\vec{I}_2\cdot\vec{J})(\vec{I}_1\cdot\vec{J}) - 2(\vec{I}_1\cdot\vec{I}_2)\vec{J}^2}{(2J+3)(2J-1)}\right] + c_4(\vec{I}_1\cdot\vec{I}_2)$$

and

$\vec{J}$ = the rotational angular momentum of the molecule
$\vec{I}_1$ = the Tl nuclear spin
$\vec{I}_2$ = the F nuclear spin
$\vec{E}$ = the external electric field
$\vec{B}$ = the external magnetic field

with[a]

$B = 6.689\,92$ GHz	$\mu_e = 4.2282(8)$ Debye[b]
$\mu_J = 35(15)$ Hz/G	$c_1/h = 126.03(12)$ kHz[b]
$\mu_1^{205} = 1.2405(3)$ kHz/G	$c_2/h = 17.89(15)$ kHz[b]
$\mu_1^{203} = 1.2285(3)$ kHz/G	$c_3/h = 0.70(3)$ kHz[b]
$\mu_2 = 2.003\,63(4)$ kHz/G	$c_4/h = -13.30(72)$ kHz.[b]

First import necessary Python packages, and define the constants.

In [1]:
```
1 import numpy as np
2 from numpy import sqrt
3 import matplotlib.pyplot as plt
```

In [26]:
```
# Units and constants

Jmax = 6      # max J value in Hamiltonian
I_Tl = 1/2    # I1 in Ramsey's notation
I_F = 1/2     # I2 in Ramsey's notation

# TlF constants. Data from D.A. Wilkening, N.F. Ramsey,
# and D.J. Larson, Phys Rev A 29, 425 (1984). Everything in Hz.

Brot = 6689920000
c1 = 126030.0
c2 = 17890.0
c3 = 700.0
c4 = -13300.0

D_TlF = 4.2282 * 0.393430307 *5.291772e-9/4.135667e-15 # [Hz/(V/cm)]

# Constants from Wilkening et al, in Hz/Gauss, for 205Tl

mu_J = 35
mu_Tl = 1240.5
mu_F = 2003.63
```

Representing the states

A state, in general, can be written as a weighted superposition of the basis states. We work in the basis $|J, m_J, I_1, m_1, I_2, m_2\rangle$.

The operations we can define on the basis states are:

- construction: e.g. calling `BasisState(QN)` creates a basis state with quantum numbers `QN = (J, mJ, I1, m1, I2, m2)`;
- equality testing;
- inner product, returning either 0 or 1;
- superposition and scalar multiplication, returning a `State` object
- a convenience function to print out all quantum numbers

In [3]:
```python
class BasisState:
    # constructor
    def __init__(self, J, mJ, I1, m1, I2, m2):
        self.J, self.mJ  = J, mJ
        self.I1, self.m1 = I1, m1
        self.I2, self.m2 = I2, m2

    # equality testing
    def __eq__(self, other):
        return self.J==other.J and self.mJ==other.mJ \
                    and self.I1==other.I1 and self.I2==other.I2 \
                    and self.m1==other.m1 and self.m2==other.m2

    # inner product
    def __matmul__(self, other):
        if self == other:
            return 1
        else:
            return 0

    # superposition: addition
    def __add__(self, other):
        if self == other:
            return State([ (2,self) ])
        else:
            return State([ (1,self), (1,other) ])

    # superposition: subtraction
    def __sub__(self, other):
        return self + -1*other

    # scalar product (psi * a)
    def __mul__(self, a):
        return State([ (a, self) ])

    # scalar product (a * psi)
    def __rmul__(self, a):
        return self * a

    def print_quantum_numbers(self):
        print( self.J,"%+d"%self.mJ,"%+0.1f"%self.m1,"%+0.1f"%self.m2 )
```

A general state `State` can have any number of components, so let's represent it as an list of pairs `(amp, psi)`, where `amp` is the relative amplitude of a component, and `psi` is a basis state. The same component must not appear twice on the list.

There are three operations we can define on the states:

- construction
- superposition: concatenate component arrays and return a `State`
- scalar multiplication `a * psi` and `psi * a`, division, negation
- component-wise inner product `psi1 @ psi2`, where `psi1` is a bra, and `psi2` a ket, returning a complex number

In addition, I define an iterator method to loop through the components, and the `__getitem__()` method to access the components (which are not necessarily in any particular order!). See Classes/Iterators (https://docs.python.org/3/tutorial/classes.html#iterators) for details.

In [4]:

```
class State:
    # constructor
    def __init__(self, data=[], remove_zero_amp_cpts=True):
        # check for duplicates
        for i in range(len(data)):
            amp1,cpt1 = data[i][0], data[i][1]
            for amp2,cpt2 in data[i+1:]:
                if cpt1 == cpt2:
                    raise AssertionError("duplicate components!")
        # remove components with zero amplitudes
        if remove_zero_amp_cpts:
            self.data = [(amp,cpt) for amp,cpt in data if amp!=0]
        else:
            self.data = data
        # for iteration over the State
        self.index = len(self.data)

    # superposition: addition
    # (highly inefficient and ugly but should work)
    def __add__(self, other):
        data = []
        # add components that are in self but not in other
        for amp1,cpt1 in self.data:
            only_in_self = True
            for amp2,cpt2 in other.data:
                if cpt2 == cpt1:
                    only_in_self = False
            if only_in_self:
                data.append((amp1,cpt1))
        # add components that are in other but not in self
        for amp1,cpt1 in other.data:
            only_in_other = True
            for amp2,cpt2 in self.data:
                if cpt2 == cpt1:
                    only_in_other = False
            if only_in_other:
                data.append((amp1,cpt1))
        # add components that are both in self and in other
        for amp1,cpt1 in self.data:
            for amp2,cpt2 in other.data:
                if cpt2 == cpt1:
                    data.append((amp1+amp2,cpt1))
        return State(data)

    # superposition: subtraction
    def __sub__(self, other):
        return self + -1*other

    # scalar product (psi * a)
    def __mul__(self, a):
        return State( [(a*amp,psi) for amp,psi in self.data] )

    # scalar product (a * psi)
    def __rmul__(self, a):
        return self * a

```

```
    # scalar division (psi / a)
    def __truediv__(self, a):
        return self * (1/a)

    # negation
    def __neg__(self):
        return -1.0 * self

    # inner product
    def __matmul__(self, other):
        result = 0
        for amp1,psi1 in self.data:
            for amp2,psi2 in other.data:
                result += amp1.conjugate()*amp2 * (psi1@psi2)
        return result

    # iterator methods
    def __iter__(self):
        return self

    def __next__(self):
        if self.index == 0:
            raise StopIteration
        self.index -= 1
        return self.data[self.index]

    # direct access to a component
    def __getitem__(self, i):
        return self.data[i]
```

Operators in Python

Define QM operators as Python functions that take `BasisState` objects, and return `State` objects. Since we are interested in finding matrix elements, we only need the action of operators on the basis states (but it'd be easy to generalize using a `for` loop).

The easiest operators to define are the diagonal ones J^2, J_z, I_{1z}, I_{2z}, which just multiply the state by their eigenvalue:

In [5]:
```
def J2(psi):
    return State([(psi.J*(psi.J+1),psi)])

def Jz(psi):
    return State([(psi.mJ,psi)])

def I1z(psi):
    return State([(psi.m1,psi)])

def I2z(psi):
    return State([(psi.m2,psi)])
```

The other angular momentum operators we can obtain through the ladder operators

$$J_\pm = J_x \pm iJ_y.$$

These are defined through their action on the basis states as (Sakurai eqns 3.5.39-40)

$$J_\pm |J,m\rangle = \sqrt{(j\mp m)(j\pm m+1)}|jm\pm 1\rangle.$$

Similarly, $I_{1\pm}, I_{2\pm}$ act on the $|I_1,m_1\rangle$ and $|I_2,m_2\rangle$ subspaces in the same way.

In [6]:
```
def Jp(psi):
    amp = sqrt((psi.J-psi.mJ)*(psi.J+psi.mJ+1))
    ket = BasisState(psi.J, psi.mJ+1, psi.I1, psi.m1, psi.I2, psi.m2)
    return State([(amp,ket)])

def Jm(psi):
    amp = sqrt((psi.J+psi.mJ)*(psi.J-psi.mJ+1))
    ket = BasisState(psi.J, psi.mJ-1, psi.I1, psi.m1, psi.I2, psi.m2)
    return State([(amp,ket)])

def I1p(psi):
    amp = sqrt((psi.I1-psi.m1)*(psi.I1+psi.m1+1))
    ket = BasisState(psi.J, psi.mJ, psi.I1, psi.m1+1, psi.I2, psi.m2)
    return State([(amp,ket)])

def I1m(psi):
    amp = sqrt((psi.I1+psi.m1)*(psi.I1-psi.m1+1))
    ket = BasisState(psi.J, psi.mJ, psi.I1, psi.m1-1, psi.I2, psi.m2)
    return State([(amp,ket)])

def I2p(psi):
    amp = sqrt((psi.I2-psi.m2)*(psi.I2+psi.m2+1))
    ket = BasisState(psi.J, psi.mJ, psi.I1, psi.m1, psi.I2, psi.m2+1)
    return State([(amp,ket)])

def I2m(psi):
    amp = sqrt((psi.I2+psi.m2)*(psi.I2-psi.m2+1))
    ket = BasisState(psi.J, psi.mJ, psi.I1, psi.m1, psi.I2, psi.m2-1)
    return State([(amp,ket)])
```

In terms of the above-defined ladder operators, we can write

$$J_x = \frac{1}{2}(J_+ + J_-); \quad J_y = \frac{1}{2i}(J_+ - J_-),$$

and similarly for I_{1x}, I_{1y} and I_{2x}, I_{2y}.

In [7]:
```
def Jx(psi):
    return .5*( Jp(psi) + Jm(psi) )

def Jy(psi):
    return -.5j*( Jp(psi) - Jm(psi) )

def I1x(psi):
    return .5*( I1p(psi) + I1m(psi) )

def I1y(psi):
    return -.5j*( I1p(psi) - I1m(psi) )

def I2x(psi):
    return .5*( I2p(psi) + I2m(psi) )

def I2y(psi):
    return -.5j*( I2p(psi) - I2m(psi) )
```

Composition of operators

All operators defined above can only accept `BasisStates` as their inputs, and they all return `States` as output. To allow composition of operators,

$$\hat{A}\hat{B}|\psi\rangle = \hat{A}(\hat{B}(|\psi\rangle)),$$

define the following function.

In [8]:
```
def com(A, B, psi):
    ABpsi = State()
    # operate with A on all components in B|psi>
    for amp,cpt in B(psi):
        ABpsi += amp * A(cpt)
    return ABpsi
```

Rotational term

The simplest term in the Hamiltonian simply gives the rotational levels:

$$H_{\mathrm{rot}} = B_{\mathrm{rot}}\vec{J}^2.$$

In [9]:
```
def Hrot(psi):
    return Brot * J2(psi)
```

Terms with ang. momentum dot products

Note that the dot product of two angular momentum operators can be written in terms of the ladder operators as

$$\vec{A}\cdot\vec{B} = A_z B_z + \frac{1}{2}(A_+ B_- + A_- B_+).$$

We have the following terms (from Table 1 of Ramsey's paper):

$$H_{c1} = c_1 \vec{I}_1 \cdot \vec{J}; \quad H_{c2} = c_2 \vec{I}_2 \cdot \vec{J}; \quad H_{c4} = c_4 \vec{I}_1 \cdot \vec{I}_2$$

$$H_{c3a} = 15c_3 \frac{(\vec{I}_1 \cdot \vec{J})(\vec{I}_2 \cdot \vec{J})}{(2J+3)(2J-1)} = \frac{15c_3}{c_1 c_2} \frac{H_{c1} H_{c2}}{(2J+3)(2J-1)}$$

$$H_{c3b} = 15c_3 \frac{(\vec{I}_2 \cdot \vec{J})(\vec{I}_1 \cdot \vec{J})}{(2J+3)(2J-1)} = \frac{15c_3}{c_1 c_2} \frac{H_{c2} H_{c1}}{(2J+3)(2J-1)}$$

$$H_{c3c} = -10c_3 \frac{(\vec{I}_1 \cdot \vec{I}_2)\vec{J}^2}{(2J+3)(2J-1)} = \frac{-10c_3}{c_4 B_{rot}} \frac{H_{c4} H_{rot}}{(2J+3)(2J-1)}$$

In [10]:
```
def Hc1(psi):
    return c1 * ( com(I1z,Jz,psi) + .5*(com(I1p,Jm,psi)+com(I1m,Jp,psi)) )

def Hc2(psi):
    return c2 * ( com(I2z,Jz,psi) + .5*(com(I2p,Jm,psi)+com(I2m,Jp,psi)) )

def Hc4(psi):
    return c4 * ( com(I1z,I2z,psi) + .5*(com(I1p,I2m,psi)+com(I1m,I2p,psi)) )

def Hc3a(psi):
    return 15*c3/c1/c2 * com(Hc1,Hc2,psi) / ((2*psi.J+3)*(2*psi.J-1))

def Hc3b(psi):
    return 15*c3/c1/c2 * com(Hc2,Hc1,psi) / ((2*psi.J+3)*(2*psi.J-1))

def Hc3c(psi):
    return -10*c3/c4/Brot * com(Hc4,Hrot,psi) / ((2*psi.J+3)*(2*psi.J-1))
```

The overall field-free Hamiltonian is

In [11]:
```
def Hff(psi):
    return Hrot(psi) + Hc1(psi) + Hc2(psi) + Hc3a(psi) + Hc3b(psi) \
            + Hc3c(psi) + Hc4(psi)
```

Zeeman Hamiltonian

In order to separate the task of finding the matrix elements and the eigenvalues, the Hamiltonian

$$H^Z = -\frac{\mu_J}{J}(\vec{J} \cdot \vec{B}) - \frac{\mu_1}{I_1}(\vec{I}_1 \cdot \vec{B}) - \frac{\mu_2}{I_2}(\vec{I}_2 \cdot \vec{B})$$

is best split into three matrices:

$$H^Z = B_x H_x^Z + B_y H_y^Z + B_z H_z^Z,$$

where

$$H_x^Z = -\frac{\mu_J}{J} J_x - \frac{\mu_1}{I_1} I_{1x} - \frac{\mu_2}{I_2} I_{2x}$$

$$H_y^Z = -\frac{\mu_J}{J}J_y - \frac{\mu_1}{I_1}I_{1y} - \frac{\mu_2}{I_2}I_{2y}$$
$$H_z^Z = -\frac{\mu_J}{J}J_z - \frac{\mu_1}{I_1}I_{1z} - \frac{\mu_2}{I_2}I_{2z}$$

Note that we are using the convention $\mu_1 = \mu_{\mathrm{Tl}}$ and $\mu_2 = \mu_{\mathrm{F}}$. The terms involving division by J are only valid for states with $J \neq 0$ (of course!).

In [12]:
```
def HZx(psi):
    if psi.J != 0:
        return -mu_J/psi.J*Jx(psi) - mu_Tl/psi.I1*I1x(psi) - mu_F/psi.I2*I2x(
    else:
        return -mu_Tl/psi.I1*I1x(psi) - mu_F/psi.I2*I2x(psi)

def HZy(psi):
    if psi.J != 0:
        return -mu_J/psi.J*Jy(psi) - mu_Tl/psi.I1*I1y(psi) - mu_F/psi.I2*I2y(
    else:
        return -mu_Tl/psi.I1*I1y(psi) - mu_F/psi.I2*I2y(psi)

def HZz(psi):
    if psi.J != 0:
        return -mu_J/psi.J*Jz(psi) - mu_Tl/psi.I1*I1z(psi) - mu_F/psi.I2*I2z(
    else:
        return -mu_Tl/psi.I1*I1z(psi) - mu_F/psi.I2*I2z(psi)
```

Stark Hamiltonian

Again splitting the Hamiltonian into the three spatial components, we have

$$H^{\mathrm{S}} = -\vec{d}\cdot\vec{E} = E_x H_x^{\mathrm{S}} + E_y H_y^{\mathrm{S}} + E_z H_z^{\mathrm{S}}.$$

To find the effect of the electric dipole operators (written in terms of the spherical harmonics)

$$\vec{d} = d_{\mathrm{TlF}}\begin{pmatrix}\hat{d}_x\\ \hat{d}_y\\ \hat{d}_z\end{pmatrix} = d_{\mathrm{TlF}}\begin{pmatrix}\sin\theta\cos\phi\\ \sin\theta\sin\phi\\ \cos\theta\end{pmatrix} = d_{\mathrm{TlF}}\sqrt{\frac{2\pi}{3}}\begin{pmatrix}Y_1^{-1} - Y_1^1\\ i(Y_1^{-1} + Y_1^1)\\ \sqrt{2}Y_1^0\end{pmatrix}$$

on the eigenstates $|J, m, \ldots\rangle$, we need to find their matrix elements. The wavefunctions are $\langle\theta,\phi|J,m\rangle = Y_J^m$, so the matrix elements of the spherical harmonics are

$$\langle J', m'|Y_1^M||J, m\rangle = \int (Y_{J'}^{m'})^* Y_1^M Y_J^m d\Omega = (-1)^m \int (Y_{J'}^{m'})^* (Y_1^{-M})^* Y_J^m d\Omega.$$

According to Wikipedia (https://en.wikipedia.org/wiki/Clebsch%E2%80%93Gordan_coefficients#Relation_to_spherical_harmc this evaluates to

$$\sqrt{\frac{2\pi}{3}}\langle J', m'|Y_1^M||J, m\rangle = (-1)^M\sqrt{\frac{(2J'+1)}{2(2J+1)}}\langle J'\ 0\ 1\ 0|J\ 0\rangle\langle J'\ m'\ 1\ -M|J\ m\rangle$$

This can be partially evaluated using the following Mathematica function:

```
coeffs[M_] := Table[(-1)^M Sqrt[(2 Jp + 1)/(2 (2 J + 1))]
    ClebschGordan[{Jp, mp}, {1, -M}, {J, m}]
    ClebschGordan[{Jp, 0}, {1, 0}, {J, 0}] // FullSimplify,
  {mp, {m - 1, m, m + 1}}, {Jp, {J - 1, J + 1}}
  ] // MatrixForm
```

The result for $M = 0$ is nonzero for $m' = m$:

$$\begin{cases} \sqrt{\dfrac{(J-m)(J+m)}{8J^2-2}} & \text{for } J' = J-1 \\ \sqrt{\dfrac{(J-m+1)(J+m+1)}{6+8J(J+2)}} & \text{for } J' = J+1 \end{cases}$$

For $M = -1$, we need $m' = m - 1$:

$$\begin{cases} -\dfrac{1}{2}\sqrt{\dfrac{(J+m)(J-1+m)}{4J^2-1}} & \text{for } J' = J-1 \\ \dfrac{1}{2}\sqrt{\dfrac{(J+1-m)(J+2-m)}{3+4J(J+2)}} & \text{for } J' = J+1 \end{cases}$$

For $M = 1$, we need $m' = m + 1$:

$$\begin{cases} -\dfrac{1}{2}\sqrt{\dfrac{(J-m)(J-1-m)}{4J^2-1}} & \text{for } J' = J-1 \\ \dfrac{1}{2}\sqrt{\dfrac{(J+1+m)(J+2+m)}{3+4J(J+2)}} & \text{for } J' = J+1 \end{cases}$$

These three cases can be written in Python as the operators:

In [13]:
```
def R10(psi):
    amp1 = sqrt((psi.J-psi.mJ)*(psi.J+psi.mJ)/(8*psi.J**2-2))
    ket1 = BasisState(psi.J-1, psi.mJ, psi.I1, psi.m1, psi.I2, psi.m2)
    amp2 = sqrt((psi.J-psi.mJ+1)*(psi.J+psi.mJ+1)/(6+8*psi.J*(psi.J+2)))
    ket2 = BasisState(psi.J+1, psi.mJ, psi.I1, psi.m1, psi.I2, psi.m2)
    return State([(amp1,ket1),(amp2,ket2)])

def R1m(psi):
    amp1 = -.5*sqrt((psi.J+psi.mJ)*(psi.J+psi.mJ-1)/(4*psi.J**2-1))
    ket1 = BasisState(psi.J-1, psi.mJ-1, psi.I1, psi.m1, psi.I2, psi.m2)
    amp2 = .5*sqrt((psi.J-psi.mJ+1)*(psi.J-psi.mJ+2)/(3+4*psi.J*(psi.J+2)))
    ket2 = BasisState(psi.J+1, psi.mJ-1, psi.I1, psi.m1, psi.I2, psi.m2)
    return State([(amp1,ket1),(amp2,ket2)])

def R1p(psi):
    amp1 = -.5*sqrt((psi.J-psi.mJ)*(psi.J-psi.mJ-1)/(4*psi.J**2-1))
    ket1 = BasisState(psi.J-1, psi.mJ+1, psi.I1, psi.m1, psi.I2, psi.m2)
    amp2 = .5*sqrt((psi.J+psi.mJ+1)*(psi.J+psi.mJ+2)/(3+4*psi.J*(psi.J+2)))
    ket2 = BasisState(psi.J+1, psi.mJ+1, psi.I1, psi.m1, psi.I2, psi.m2)
    return State([(amp1,ket1),(amp2,ket2)])
```

In terms of the operators

$$R_1^M \equiv \sqrt{\frac{2\pi}{3}} Y_1^M$$

and the molecular dipole moment d_{TlF}, the three Stark Hamiltonians are

$$\begin{aligned} H_x^{\mathrm{S}} &= -d_{\mathrm{TlF}}(R_1^{-1} - R_1^1) \\ H_y^{\mathrm{S}} &= -d_{\mathrm{TlF}}\, i(R_1^{-1} + R_1^1) \\ H_z^{\mathrm{S}} &= -d_{\mathrm{TlF}}\sqrt{2}R_1^0 \end{aligned}$$

In Python:

In [14]:
```
def HSx(psi):
    return -D_TlF * ( R1m(psi) - R1p(psi) )

def HSy(psi):
    return -D_TlF * 1j * ( R1m(psi) + R1p(psi) )

def HSz(psi):
    return -D_TlF * sqrt(2)*R10(psi)
```

An alternative c_3 term

The c_3 term in Ramsey's Hamiltonian assumes that J is a good quantum number, which breaks down at high E field. From Wikipedia (https://en.wikipedia.org/wiki/Hyperfine_structure#Molecular_hyperfine_structure), we get the term

$$H_{\mathrm{c3}}^{\mathrm{alt}} = \frac{5}{2}c_3 \left[2\vec{I}_1\vec{I}_2 - 3(\vec{I}_1\cdot\hat{\vec{R}})(\vec{I}_2\cdot\hat{\vec{R}}) - 3(\vec{I}_2\cdot\hat{\vec{R}})(\vec{I}_1\cdot\hat{\vec{R}}) \right].$$

Write the dot products in the form

$$\begin{aligned} H_{\mathrm{I1R}} &= \vec{I}_1\cdot\hat{\vec{R}} = I_{1z}R_1^0 + \frac{1}{2}(I_{1+}R_1^{-1} + I_{1-}R_1^1) \\ H_{\mathrm{I2R}} &= \vec{I}_2\cdot\hat{\vec{R}} = I_{2z}R_1^0 + \frac{1}{2}(I_{2+}R_1^{-1} + I_{2-}R_1^1), \end{aligned}$$

as follows:

In [15]:
```
def HI1R(psi):
    return com(I1z,R10,psi) + .5*(com(I1p,R1m,psi)+com(I1m,R1p,psi))

def HI2R(psi):
    return com(I2z,R10,psi) + .5*(com(I2p,R1m,psi)+com(I2m,R1p,psi))
```

The c_3 term becomes

$$H_{\mathrm{c3}}^{\mathrm{alt}} = \frac{5}{2}c_3 \left[\frac{2}{c_4}H_{\mathrm{c4}} - 3H_{\mathrm{I1R}}H_{\mathrm{I2R}} - 3H_{\mathrm{I2R}}H_{\mathrm{I1R}} \right].$$

In Python:

In [16]:
```
def Hc3_alt(psi):
    return 5*c3/c4*Hc4(psi) - 15*c3/2*(com(HI1R,HI2R,psi)+com(HI2R,HI1R,psi))
```

The corresponding alternative field-free Hamiltonian is

In [17]:
```
def Hff_alt(psi):
    return Hrot(psi) + Hc1(psi) + Hc2(psi) + Hc3_alt(psi) + Hc4(psi)
```

Finding the matrix elements

With all the operators defined, we can evaluate the matrix elements for a given range of quantum numbers. Write down the basis as a list of `BasisState` components:

In [18]:
```
QN = np.array([BasisState(J,mJ,I_Tl,m1,I_F,m2)
      for J in range(Jmax+1)
      for mJ in range(-J,J+1)
      for m1 in np.arange(-I_Tl,I_Tl+1)
      for m2 in np.arange(-I_F,I_F+1)])
```

The field-free and Stark/Zeeman components of the Hamiltonian then have the matrix elements

In [19]:
```
%%time

def HMatElems(H, QN):
    result = np.empty((len(QN),len(QN)), dtype=complex)
    for i,a in enumerate(QN):
        for j,b in enumerate(QN):
            result[i,j] = (1*a)@H(b)
    return result

Hff_m = HMatElems(Hff, QN)
HSx_m = HMatElems(HSx, QN)
HSy_m = HMatElems(HSy, QN)
HSz_m = HMatElems(HSz, QN)
HZx_m = HMatElems(HZx, QN)
HZy_m = HMatElems(HZy, QN)
HZz_m = HMatElems(HZz, QN)
```

```
Wall time: 1min 2s
```

Find the energies

Above, we have evaluated the matrix elements for the zero-field Hamiltonian H_{ff}, as well as the $\vec{E} = 1 = \vec{B}$ cases. For general fields $\vec{E}, \vec{B}$, the Hamiltonian is

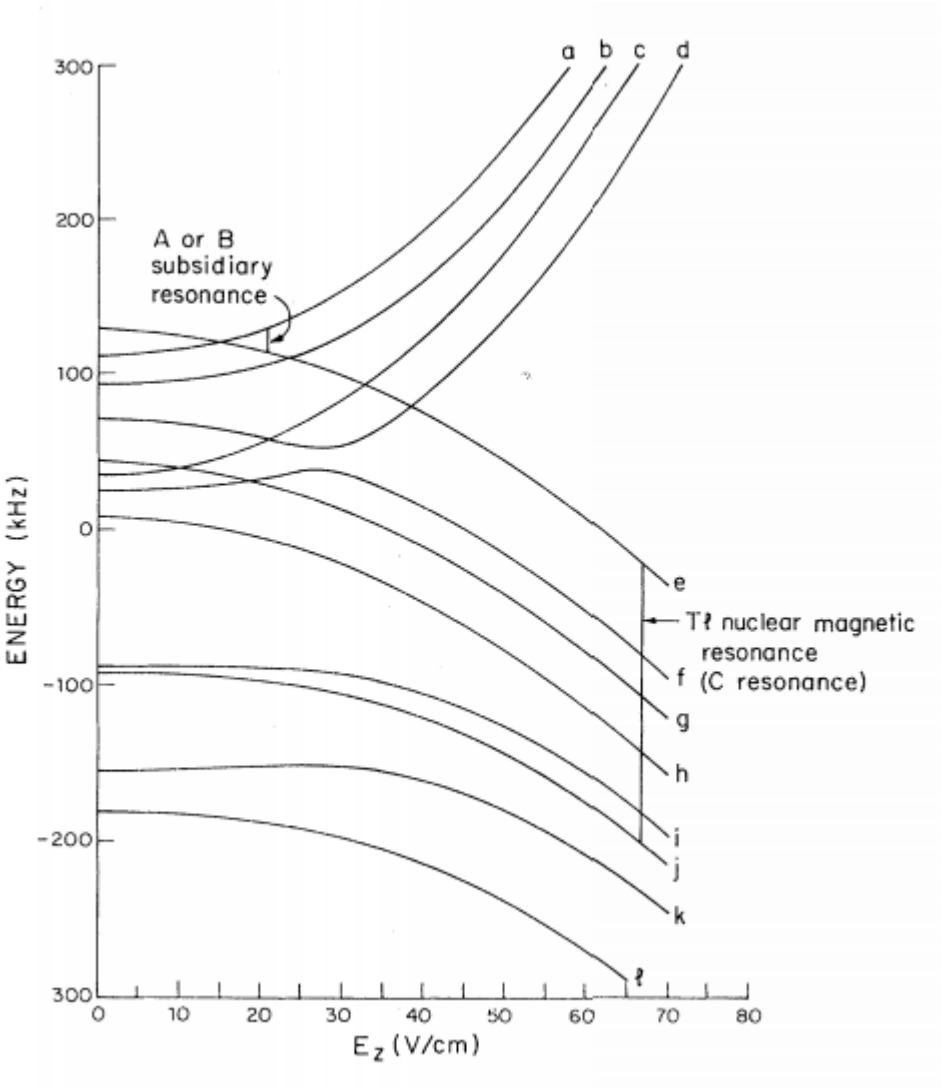
$$H = H_{\mathrm{ff}} + \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \cdot \begin{pmatrix} H_x^{\mathrm{S}} \\ H_y^{\mathrm{S}} \\ H_z^{\mathrm{S}} \end{pmatrix} + \begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix} \cdot \begin{pmatrix} H_x^{\mathrm{Z}} \\ H_y^{\mathrm{Z}} \\ H_z^{\mathrm{Z}} \end{pmatrix}.$$

When looking at the Zeeman/Stark effects on the hyperfine structure, the rotational structure is not of interest, so I subtract it for clarity in the following `spectrum()` function. It evaluates the above Hamiltonian for each point on the array of fields, and returns a list of energy levels, sorted by size:

In [20]:
```
def spectrum(Ex_arr,Ey_arr,Ez_arr,Bx_arr,By_arr,Bz_arr):
    energies_arr = []
    for Ex,Ey,Ez,Bx,By,Bz in zip(Ex_arr,Ey_arr,Ez_arr,Bx_arr,By_arr,Bz_arr):
        HamE = Hff_m + \
            Ex*HSx_m  + Ey*HSy_m + Ez*HSz_m + \
            Bx*HZx_m  + By*HZy_m + Bz*HZz_m
        D = np.sort(np.linalg.eigvalsh(HamE))

        # Subtract away rotational energy for easier viewing of substructure
        hfs_mat = []
        for i,psi in enumerate(QN):
            hfs_mat.append(D[i] - psi.J*(psi.J +1)*Brot)
        hfs_kHz = np.array(hfs_mat)/1000

        energies_arr.append(hfs_kHz)
    return np.array(energies_arr)
```

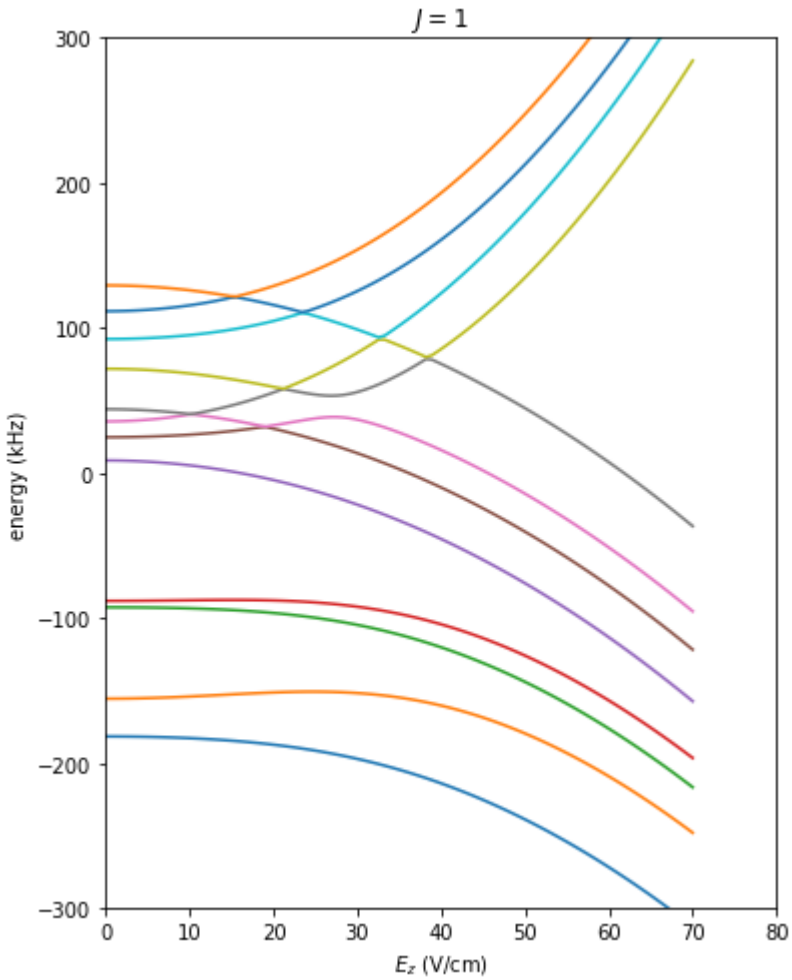
Test 1: Reproducing Ramsey's Fig. 4

That's how it's supposed to look at 18.4 gauss of B_z:



Evaluate find the energies for B_z of 18.4 gauss, and E_z between 0 and 70 V/cm, and plot the result:

In [21]:
```
Ez = np.linspace(0,70,100)
Bz = 18.4 * np.ones(Ez.shape)
Ex = np.zeros(Ez.shape)
Ey = np.zeros(Ez.shape)
Bx = np.zeros(Ez.shape)
By = np.zeros(Ez.shape)

energies = spectrum(Ex,Ey,Ez,Bx,By,Bz)

for i in range(4,16):
    plt.plot(Ez, energies.T[i])

plt.title("$J=1$")
plt.xlabel("$E_z$ (V/cm)")
plt.ylabel("energy (kHz)")

plt.xlim([0,80])
plt.ylim([-300,300])

fig = plt.gcf()
fig.set_size_inches(6, 8)
plt.show()
```



Test 2: Rotating the fields

We have seen that the z components of electric and magnetic field reproduce Ramsey's result. (They also match the energy levels calculated by Dave DeMille's Matlab code modulo a typo in his `c3` term.)

We should be able to get the same energy levels if we rotate both the electric and the magnetic field by the same angle. Define the rotation matrices:

In [22]:
```
def Rx(theta):
    return np.array([[1,0,0],
                     [0,np.cos(theta),-np.sin(theta)],
                     [0,np.sin(theta),np.cos(theta)]])

def Ry(theta):
    return np.array([[np.cos(theta),0,np.sin(theta)],
                     [0,1,0],
                     [-np.sin(theta),0,np.cos(theta)]])

def Rz(theta):
    return np.array([[np.cos(theta),-np.sin(theta),0],
                     [np.sin(theta),np.cos(theta),0],
                     [0,0,1]])
```

Start with a constant B_x and a varying E_x. Calculate the energies:

In [23]:
```
Ex = np.linspace(0,70,100)
Ey = np.zeros(Ex.shape)
Ez = np.zeros(Ex.shape)

Bx = 18.4*np.ones(Ez.shape)
By = np.zeros(Ex.shape)
Bz = np.zeros(Ex.shape)

energies0 = spectrum(Ex,Ey,Ez,Bx,By,Bz)
```

Rotate both fields by $R_y(\theta)R_z(\phi)$ and calculate the energy difference:

In [24]:
```
print("theta\t phi\t delta")

for theta in np.pi/180*np.linspace(10,99,4):
    for phi in np.pi/180*np.linspace(10,99,4):
        # rotate fields
        Exr,Eyr,Ezr = Ry(theta)@Rz(phi)@np.array([Ex,Ey,Ez])
        Bxr,Byr,Bzr = Ry(theta)@Rz(phi)@np.array([Bx,By,Bz])

        # calculate energy difference
        energies1 = spectrum(Exr,Eyr,Ezr,Bxr,Byr,Bzr)
        print("%0.2f" % (theta*180/np.pi),
              "\t", "%0.2f" % (phi*180/np.pi),
              "\t", "%0.3E" % np.sum(energies0-energies1))
```

```
theta    phi     delta
10.00    10.00   -4.518E-05
10.00    39.67   4.793E-05
10.00    69.33   1.702E-05
10.00    99.00   2.812E-06
39.67    10.00   6.701E-06
39.67    39.67   8.797E-06
39.67    69.33   -1.672E-06
39.67    99.00   5.121E-06
69.33    10.00   -3.258E-05
69.33    39.67   -5.852E-05
69.33    69.33   3.559E-05
69.33    99.00   -4.242E-05
99.00    10.00   -3.176E-05
99.00    39.67   -2.792E-05
99.00    69.33   -2.715E-05
99.00    99.00   -3.482E-05
```

Identifying the eigenstates

We can also obtain the eigenvectors corresponding to the energies, which allows us to extract the quantum numbers corresponding to each energy level.

The function `eigenstates()` will return the energies and eigenstates (as an array of `State` objects) at a given EM field strength, ignoring components with amplitudes less than `epsilon`. Note that the amplitudes of the components of the eigenstates will lose all phase information to

facilitate sorting. Unlike `spectrum()`, which takes arrays of field strength, `eigenstates()` only accepts a single field strength.

In [25]:
```
def eigenstates(Ex,Ey,Ez,Bx,By,Bz,epsilon=1e-6):
    # diagonalize the Hamiltonian
    H = Hff_m \
        + Ex*HSx_m + Ey*HSy_m + Ez*HSz_m \
        + Bx*HZx_m + By*HZy_m + Bz*HZz_m
    eigvals,eigvecs = np.linalg.eigh(H)

    # find the quantum numbers of the largest-|amplitude| components
    states = []
    for eigvec in eigvecs.T:
        # normalize the largest |amplitude| to 1
        eigvec = eigvec / np.max(np.abs(eigvec))
        # find indices of the largest-|amplitude| components
        major = np.abs(eigvec) > epsilon

        # collect the major components into a State
        eigenstate = State()
        for amp,psi in zip(eigvec[major], QN[major]):
            eigenstate += amp * psi

        # sort the components by decreasing |amplitude|
        amps = np.array(eigenstate.data).T[0]
        cpts = np.array(eigenstate.data).T[1]
        cpts = cpts[np.argsort(np.abs(amps))]
        amps = amps[np.argsort(np.abs(amps))]
        sorted_state = State( data=np.array((amps,cpts)).T )
        states.append(sorted_state)

    return eigvals, np.array(states)
```

The convenience function `major_eigenstates()` prints out the energies and quantum numbers for a specified J (by default, for $J = 1$), ignoring components less than `epsilon` (by default, `epsilon=.95`).

Note that J is determined simply from the order of energies, i.e. $J = 0$ corresponds to the first four states, instead of through the eigenvector's components. This is convenient at high fields, where J ceases to be a good quantum number but can still be used to identify the states in an asymptotic sense.

Similarly, `largest_eigenstate()` prints out a table of energies and quantum numbers, for only a single component for each eigenstate.

In [26]:
```
def largest_eigenstate(Ex,Ey,Ez,Bx,By,Bz,J=1,epsilon=.95):
    energies, states = eigenstates(Ex,Ey,Ez,Bx,By,Bz,epsilon=epsilon)
    print("E [kHz]\t J, mJ, m1, m2\n-----------------------")
    for i in reversed(np.arange((2*I_Tl+1)*(2*I_F+1)*J**2,(2*I_Tl+1)*(2*I_F+1
        print("%+0.2f" % ((energies[int(i)]-J*(J+1)*Brot)/1e3), end='\t ')
        states[int(i)][0][1].print_quantum_numbers()

def major_eigenstates(Ex,Ey,Ez,Bx,By,Bz,J=1,epsilon=.95):
    energies, states = eigenstates(Ex,Ey,Ez,Bx,By,Bz,epsilon=epsilon)
    for i in reversed(np.arange((2*I_Tl+1)*(2*I_F+1)*J**2,(2*I_Tl+1)*(2*I_F+1
        print("E = %+0.16e" % ((energies[int(i)]-J*(J+1)*Brot)/1e3),"kHz",end
        for amp,psi in states[int(i)]:
            print("\t%+0.3f"%np.real(amp),"%+0.3fi"%np.imag(amp), end=' ')
            psi.print_quantum_numbers()
```

Test 3: Low-field state identification

The $J = 1$ levels (with applied fields) will have the quantum numbers as given in Ramsey's Table 2:

Level	$\lvert m_J, m_1, m_2 \rangle$
a	$\lvert 0, -\frac{1}{2}, -\frac{1}{2} \rangle$
b	$\lvert 0, +\frac{1}{2}, -\frac{1}{2} \rangle$
c	$\lvert 0, -\frac{1}{2}, +\frac{1}{2} \rangle$
d	$\lvert 0, +\frac{1}{2}, +\frac{1}{2} \rangle$
e	$\lvert -1, -\frac{1}{2}, -\frac{1}{2} \rangle$
f	$\lvert +1, +\frac{1}{2}, -\frac{1}{2} \rangle$
g	$\lvert -1, -\frac{1}{2}, +\frac{1}{2} \rangle$
h	$\lvert +1, +\frac{1}{2}, +\frac{1}{2} \rangle$
i	$\lvert +1, -\frac{1}{2}, -\frac{1}{2} \rangle$
j	$\lvert -1, +\frac{1}{2}, -\frac{1}{2} \rangle$
k	$\lvert +1, -\frac{1}{2}, +\frac{1}{2} \rangle$
l	$\lvert -1, +\frac{1}{2}, +\frac{1}{2} \rangle$

The function `largest_eigenstate()` defined above can be used to obtain the same prediction:

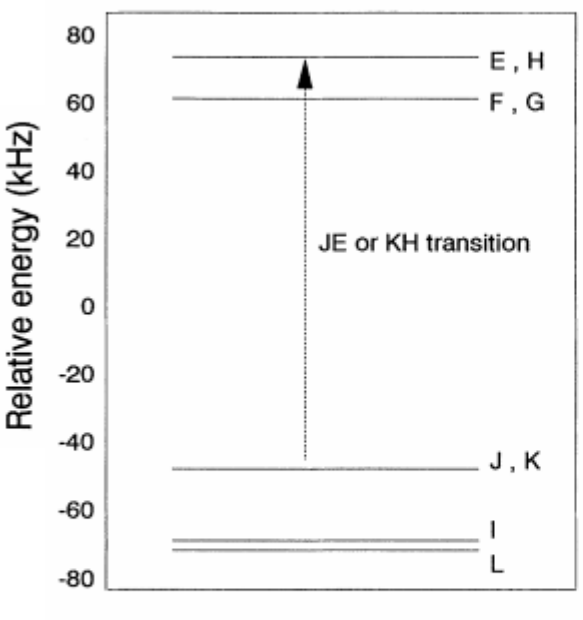
In [27]:
```
1 largest_eigenstate(0,0,70,0,0,18.4,J=1)
```

```
E [kHz]  J, mJ, m1, m2
-----------------------
+401.16  1 +0 -0.5 -0.5
+364.60  1 +0 +0.5 -0.5
+334.26  1 +0 -0.5 +0.5
+284.15  1 +0 +0.5 +0.5
-36.60   1 -1 -0.5 -0.5
-95.30   1 +1 +0.5 -0.5
-121.72  1 -1 -0.5 +0.5
-157.27  1 +1 +0.5 +0.5
-196.39  1 +1 -0.5 -0.5
-216.56  1 -1 +0.5 -0.5
-247.92  1 +1 -0.5 +0.5
-312.48  1 -1 +0.5 +0.5
```

Test 4: High-field state identification

At high fields, the rotational angular momentum J is no longer a good quantum number, but we can still use it in an asymptotic sense to identify the 4th through 15th lowest eigenstate. Consider Fig. 7 and Table 1 of Hinds's paper:

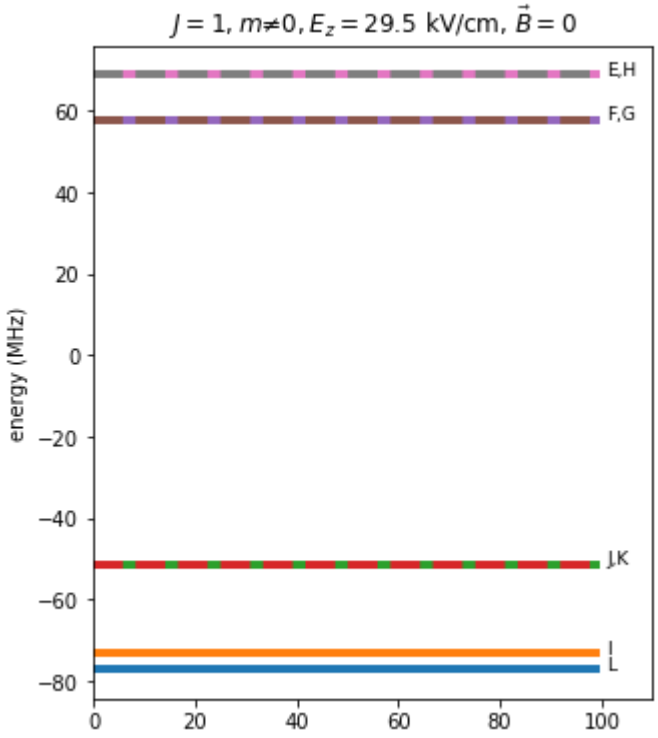
Cho, Donghyun, K. Sangster, and E. A. Hinds. "Search for time-reversal-symmetry violation in thallium fluoride using a jet source." Physical Review A **44**, no. 5 (1991): 2783. (https://journals.aps.org/pra/abstract/10.1103/PhysRevA.44.2783)



Label	$\lvert M_J, M_1, M_2 \rangle$
A	$\left\lvert 0, -\frac{1}{2}, -\frac{1}{2} \right\rangle$
B	$\frac{1}{\sqrt{2}} \left\lvert 0, +\frac{1}{2}, -\frac{1}{2} \right\rangle - \frac{1}{\sqrt{2}} \left\lvert 0, -\frac{1}{2}, +\frac{1}{2} \right\rangle$
C	$\frac{1}{\sqrt{2}} \left\lvert 0, +\frac{1}{2}, -\frac{1}{2} \right\rangle + \frac{1}{\sqrt{2}} \left\lvert 0, -\frac{1}{2}, +\frac{1}{2} \right\rangle$
D	$\left\lvert 0, +\frac{1}{2}, +\frac{1}{2} \right\rangle$
E	$\left\lvert -1, -\frac{1}{2}, -\frac{1}{2} \right\rangle$
F	$\left\lvert +1, +\frac{1}{2}, -\frac{1}{2} \right\rangle$
G	$\left\lvert -1, -\frac{1}{2}, +\frac{1}{2} \right\rangle$
H	$\left\lvert +1, +\frac{1}{2}, +\frac{1}{2} \right\rangle$
I	$\frac{1}{\sqrt{2}} \left\lvert +1, -\frac{1}{2}, -\frac{1}{2} \right\rangle + \frac{1}{\sqrt{2}} \left\lvert -1, +\frac{1}{2}, +\frac{1}{2} \right\rangle$
J	$\left\lvert -1, +\frac{1}{2}, -\frac{1}{2} \right\rangle$
K	$\left\lvert +1, -\frac{1}{2}, +\frac{1}{2} \right\rangle$
L	$\frac{1}{\sqrt{2}} \left\lvert +1, -\frac{1}{2}, -\frac{1}{2} \right\rangle - \frac{1}{\sqrt{2}} \left\lvert -1, +\frac{1}{2}, +\frac{1}{2} \right\rangle$

The above plot is readily reproduced:

In [28]:
```
energies, _ = eigenstates(0,0,29.5e3,0,0,0,epsilon=.95)

energies /= 1e3
epsilon = 1e-3
En = np.ones(100)
mean = np.mean(energies[4:12])
labels = ["L","I","J,K",1,"F,G",1,"E,H"]
for i,E in enumerate(energies[4:12]):
    if np.abs(E-energies[4+i-1]) < epsilon:
        plt.plot(E*En-mean, lw=4, ls='dashed')
    else:
        plt.plot(E*En-mean, lw=4)
        plt.text(101,E-mean,labels[i],fontsize=9)
plt.title(r"$J=1, m\ne0, E_z=29.5$ kV/cm, $\vec B=0$")
plt.ylabel("energy (MHz)")
plt.xlim([0,110])
fig = plt.gcf()
fig.set_size_inches(5, 6)
plt.show()
```



As explained in the figure's caption in the paper, the pairs (E, H), (F, G), and (J, K) are degenerate doublets, while I and L are split. The function `major_eigenstates()` can give the eigencomponents of these energy levels:

In [29]:
```
1 major_eigenstates(0,0,29.5e3,0,0,0,J=1,epsilon=.5)
```

```
E = -6.1639749832001876e+05 kHz
        -1.000 +0.000i 2 +0 -0.5 +0.5
        +1.000 +0.000i 2 +0 +0.5 -0.5
        +0.889 +0.000i 0 +0 -0.5 +0.5
        -0.889 +0.000i 0 +0 +0.5 -0.5
        -0.541 +0.000i 3 +0 -0.5 +0.5
        +0.541 +0.000i 3 +0 +0.5 -0.5
E = -6.1641014898880199e+05 kHz
        -1.000 +0.000i 2 +0 +0.5 -0.5
        -1.000 +0.000i 2 +0 -0.5 +0.5
        +0.889 +0.000i 0 +0 +0.5 -0.5
        +0.889 +0.000i 0 +0 -0.5 +0.5
        -0.541 +0.000i 3 +0 +0.5 -0.5
        -0.541 +0.000i 3 +0 -0.5 +0.5
E = -6.1641112293604854e+05 kHz
        -1.000 +0.000i 2 +0 -0.5 -0.5
        +0.889 +0.000i 0 +0 -0.5 -0.5
        -0.541 +0.000i 3 +0 -0.5 -0.5
E = -6.1641112293609045e+05 kHz
        -1.000 +0.000i 2 +0 +0.5 +0.5
        +0.889 +0.000i 0 +0 +0.5 +0.5
        -0.541 +0.000i 3 +0 +0.5 +0.5
E = -2.1313743032864347e+07 kHz
        -1.000 +0.000i 1 +1 +0.5 +0.5
        -0.759 +0.000i 2 +1 +0.5 +0.5
E = -2.1313743032864448e+07 kHz
        -1.000 +0.000i 1 -1 -0.5 -0.5
        -0.759 +0.000i 2 -1 -0.5 -0.5
E = -2.1313754065739054e+07 kHz
        +1.000 +0.000i 1 -1 -0.5 +0.5
        +0.759 +0.000i 2 -1 -0.5 +0.5
E = -2.1313754065739192e+07 kHz
        -1.000 +0.000i 1 +1 +0.5 -0.5
        -0.759 +0.000i 2 +1 +0.5 -0.5
E = -2.1313863046818659e+07 kHz
        -1.000 +0.000i 1 -1 +0.5 -0.5
        -0.759 +0.000i 2 -1 +0.5 -0.5
E = -2.1313863046818767e+07 kHz
        +1.000 +0.000i 1 +1 -0.5 +0.5
        +0.759 +0.000i 2 +1 -0.5 +0.5
E = -2.1313885096213862e+07 kHz
        +1.000 +0.000i 1 -1 +0.5 +0.5
        +1.000 +0.000i 1 +1 -0.5 -0.5
        +0.759 +0.000i 2 -1 +0.5 +0.5
        +0.759 +0.000i 2 +1 -0.5 -0.5
E = -2.1313888809510924e+07 kHz
        +1.000 +0.000i 1 +1 -0.5 -0.5
        -1.000 +0.000i 1 -1 +0.5 +0.5
        +0.759 +0.000i 2 +1 -0.5 -0.5
        -0.759 +0.000i 2 -1 +0.5 +0.5
```

These states plotted in the above graph match the states in Ed Hinds's Table 1. Note that J is no longer a good quantum number.