■ Concepts and Methods of 2D Infrared Spectroscopy
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This progam was used to produce Figs. 4.14 and 10.8.

Number of single excited states, and their frequencies and transition dipoles, taken from the Gaussian output. An offset-frequency is subtracted (and added back in after the Fouriertransform) to save computation time. The two transition dipoles are in the x- and y-axis, respectively.

```
In[1]:= n = 2;
        w = {1889.184, 1947.621};
        mu = {Sqrt[.908] {1., 0, 0}, Sqrt[.671] {0, 1., 0}};
        woff = 1915;
        w -= woff;
```

Number of double excited states, and their frequencies and transition dipoles, taken from the Gaussian output. We use the harmonic approximation for the transition dipoles.

```
In[6]:= n2 = 3;
        w2 = {3767.517, 3883.911, 3813.698};
        w2 -= 2 woff;
        mu2 = {{Sqrt[2] mu[[1]], {0, 0, 0}, mu[[2]]}, {{0, 0, 0}, Sqrt[2] mu[[2]], mu[[1]]}};
```

Parameters and constants

```
In[10]:= nt = 128;
         dt = 0.25;
         T2 = 2.;
         c = .188;
         t2 = 0;
```

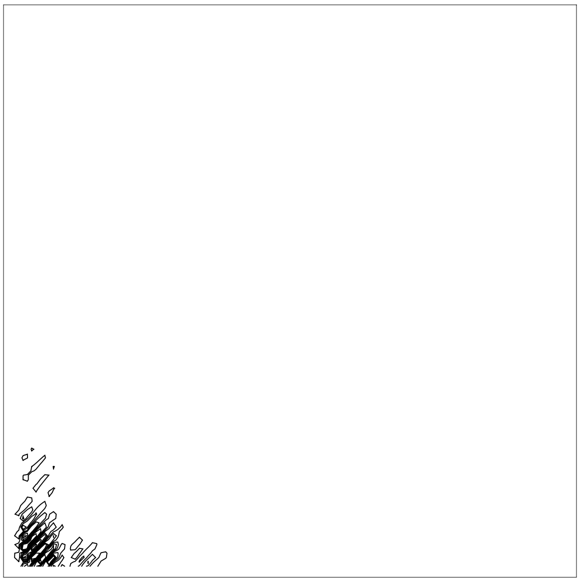
Calculate response functions for rephasing and non-rephasing diagrams (Eqs. 10.11, 10.12, and 10.13). The first time-point needs to be halved (Sect.9.5.3).

```
In[27]:= Rr = Table[0., {it1, 1, nt}, {it3, 1, nt}];
         Rnr = Table[0., {it1, 1, nt}, {it3, 1, nt}];
         For[j = 1, j ≤ n, j++,
          For[i = 1, i ≤ n, i++,
           mui = Sqrt[mu[[i]].mu[[i]]];
           muj = Sqrt[mu[[j]].mu[[j]]];
           cos1 = mu[[i]].mu[[j]] / mui / muj;
           angle = (1 + 2 cos1^2) / 15;
           dipole = mui^2 * muj^2;
           (*Rephasing diagram R1*)
           Rr -= dipole angle Table[Exp[+I w[[j]] c (it1 - 1) dt - I w[[i]] c (it3 - 1) dt +
                I (w[[j]] - w[[i]]) c t2 - (it1 + it3 - 2) dt / T2] , {it1, 1, nt}, {it3, 1, nt}];
           (*Rephasing diagram R2*)
           Rr -= dipole angle
             Table[Exp[+I w[[j]] c (it1 - 1) dt - I w[[i]] c (it3 - 1) dt - (it1 + it3 - 2) dt / T2] ,
              {it1, 1, nt}, {it3, 1, nt}];
```

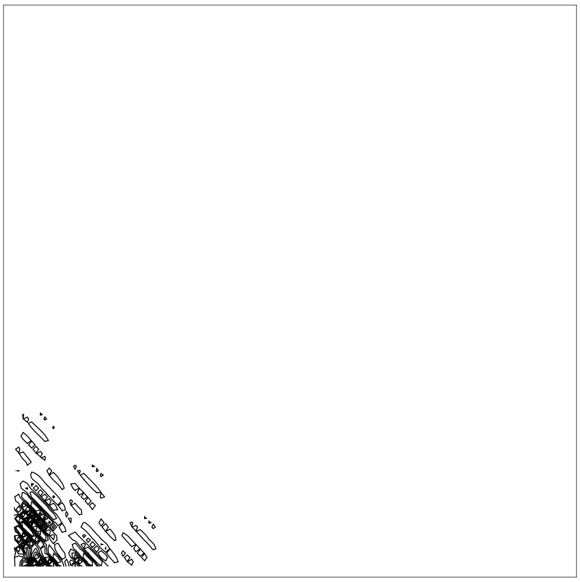
```
   For[k = 1, k ≤ n2, k++,
    mujk = Sqrt[mu2[[j, k]].mu2[[j, k]]];
    muik = Sqrt[mu2[[i, k]].mu2[[i, k]]];
    dipole = mui * muj * muik * mujk;
    cos2 = If[muik ≠ 0 && mujk ≠ 0, mu2[[i, k]].mu2[[j, k]] / muik / mujk, 0];
    cos3 = If[muik ≠ 0 , mu[[i]].mu2[[i, k]] / mui / muik, 0];
    cos4 = If[mujk ≠ 0, mu[[j]].mu2[[j, k]] / muj / mujk, 0];
    cos5 = If[mujk ≠ 0, mu[[i]].mu2[[j, k]] / mui / mujk, 0];
    cos6 = If[muik ≠ 0 , mu[[j]].mu2[[i, k]] / muj / muik, 0];
    angle = (cos1 cos2 + cos3 cos4 + cos5 cos6) / 15;
    (*Rephasing diagram R3*)
    Rr +=
     angle dipole Table[Exp[+I w[[j]] c (it1 - 1) dt - I (w2[[k]] - w[[j]]) c (it3 - 1) dt +
         I (w[[j]] - w[[i]]) c t2 - (it1 + it3 - 2) dt / T2] , {it1, 1, nt}, {it3, 1, nt}];
   ]
  ]
 ]

 For[j = 1, j ≤ n, j++,
  For[i = 1, i ≤ n, i++,
   mui = Sqrt[mu[[i]].mu[[i]]];
   muj = Sqrt[mu[[j]].mu[[j]]];
   cos1 = mu[[i]].mu[[j]] / mui / muj;
   angle = (1 + 2 cos1^2) / 15;
   (*Non-rephasing diagram R4*)
   Rnr -= dipole angle Table[Exp[-I w[[j]] c (it1 - 1) dt - I w[[j]] c (it3 - 1) dt -
        I (w[[j]] - w[[i]]) c t2 - (it1 + it3 - 2) dt / T2] , {it1, 1, nt}, {it3, 1, nt}];
   (*Non-rephasing Diagram R5*)
   Rnr -= dipole angle
     Table[Exp[-I w[[j]] c (it1 - 1) dt - I w[[i]] c (it3 - 1) dt - (it1 + it3 - 2) dt / T2] ,
      {it1, 1, nt}, {it3, 1, nt}];
   For[k = 1, k ≤ n2, k++,
    mujk = Sqrt[mu2[[j, k]].mu2[[j, k]]];
    muik = Sqrt[mu2[[i, k]].mu2[[i, k]]];
    dipole = mui * muj * muik * mujk;
    cos2 = If[muik ≠ 0 && mujk ≠ 0, mu2[[i, k]].mu2[[j, k]] / muik / mujk, 0];
    cos3 = If[muik ≠ 0 , mu[[i]].mu2[[i, k]] / mui / muik, 0];
    cos4 = If[mujk ≠ 0, mu[[j]].mu2[[j, k]] / muj / mujk, 0];
    cos5 = If[mujk ≠ 0, mu[[i]].mu2[[j, k]] / mui / mujk, 0];
    cos6 = If[muik ≠ 0 , mu[[j]].mu2[[i, k]] / muj / muik, 0];
    angle = (cos1 cos2 + cos3 cos4 + cos5 cos6) / 15;
    (*Non-rephasing diagram R6*)
    Rnr +=
     angle dipole Table[Exp[-I w[[j]] c (it1 - 1) dt - I (w2[[k]] - w[[i]]) c (it3 - 1) dt -
         I (w[[j]] - w[[i]]) c t2 - (it1 + it3 - 2) dt / T2] , {it1, 1, nt}, {it3, 1, nt}];
   ]
  ]
 ]
 For[i = 1, i ≤ nt, i++, Rnr[[i, 1]] /= 2; Rr[[i, 1]] /= 2];
 For[i = 2, i ≤ nt, i++, Rnr[[1, i]] /= 2; Rr[[1, i]] /= 2];
```

Plot time-domain data

```
In[33]:= ListContourPlot[Re[Rr], PlotRange → All, Contours → 10,
          ContourShading → False, FrameTicks → None, FrameLabel → {t3, t1}]
         ListContourPlot[Re[Rnr], PlotRange → All, Contours → 10,
          ContourShading → False, FrameTicks → None, FrameLabel → {t3, t1}]
```




```
Out[33]= - ContourGraphics -
```




```
Out[34]= - ContourGraphics -
```

Perform 2D Fourier transform and re-order data so that w1=w3=0 is centerd in the middle. Frequency axis w1 is inverted.

```
In[35]:= spectrum2Dr = Fourier[Rr];
         spectrum2Dr = Reverse[Drop[RotateRight[spectrum2Dr, {nt / 2, nt / 2}], 1, 1]];

         spectrum2Dnr = Fourier[Rnr];
         spectrum2Dnr = Drop[RotateRight[spectrum2Dnr, {nt / 2, nt / 2}], 1, 1];

         spectrum2Dabs = Re[spectrum2Dr + spectrum2Dnr];
```

Plot purely absorptive spectrum

```
In[55]:= ticks = Table[{ (w - woff) * .188 * nt * dt / 2 / Pi + nt / 2, w}, {w, 1800, 2000, 50}];
         max = Max[{Max[spectrum2Dabs], -Min[spectrum2Dabs]}];
         p1 = ListContourPlot[spectrum2Dabs,
            PlotRange → {0, max}, ContourShading → False, Contours → 20, Ticks → None,
            ContourStyle → {RGBColor[0, 0, 1]}, DisplayFunction -> Identity];
         p2 = ListContourPlot[spectrum2Dabs, PlotRange → {-max, 0},
            ContourShading → False, Contours → 20, Ticks → None,
            ContourStyle → {RGBColor[1, 0, 0]}, DisplayFunction -> Identity];
         Show[{p1, p2}, FrameTicks → {ticks, ticks, None, None},
           PlotRange → {{1, nt - 1}, {1, nt - 1}}, DisplayFunction → $DisplayFunction];
```