H2 molecule

Hamiltonian of H_2^+ molecule is

$$H = -\frac{\hbar\nabla^2}{2m} - \frac{q^2}{4\pi\epsilon_0 r_1} - \frac{q^2}{4\pi\epsilon_0 r_2} + \frac{q^2}{4\pi\epsilon_0 R} \tag{1}$$

Let's introduce dimensionless units

$$\frac{H}{Ry} \rightarrow H \tag{2}$$

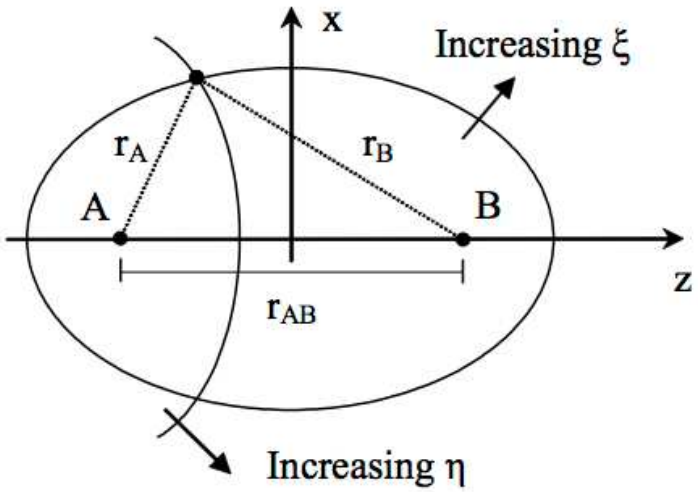
$$r_B^2\nabla^2 \rightarrow \nabla^2 \tag{3}$$

$$(\frac{r_1}{r_B}, \frac{r_2}{r_B}, \frac{R}{r_B}) \rightarrow (r_1, r_2, R) \tag{4}$$

using Hydrogen energy $Ry = \frac{mq^4}{8h^2\epsilon_0^2}$ and Bohr radius $r_B = \frac{4\pi\epsilon_0\hbar^2}{mq^2}$. We get

$$H = -\nabla^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{R}. \tag{5}$$

We will use prolate coordinate system (`http://en.wikipedia.org/wiki/Prolate_spheroidal_coordinates`), in which the Hamiltonian of the dimers leads to a separable diff. equation.



The prolate coordinate system is defined by (see Wikipedia):

$$\xi = \frac{r_1 + r_2}{R} \tag{6}$$

$$\eta = \frac{r_1 - r_2}{R} \tag{7}$$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \frac{R}{2}\sqrt{\xi^2 - 1}\sqrt{1 - \eta^2}\cos\phi \\ \frac{R}{2}\sqrt{\xi^2 - 1}\sqrt{1 - \eta^2}\sin\phi \\ \frac{R}{2}\xi\eta \end{pmatrix} \tag{8}$$

$$dV = \left(\frac{R}{2}\right)^3 (\xi^2 - \eta^2) d\xi d\eta d\phi \tag{9}$$

$$\eta \in [-1,1] \quad and \quad \xi \in [1,\infty] \tag{10}$$

$$\nabla^2 = \frac{4}{R^2(\xi^2-\eta^2)}\left[\frac{\partial}{\partial\xi}(\xi^2-1)\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}(1-\eta^2)\frac{\partial}{\partial\eta} + \frac{1}{\xi^2-1}\frac{\partial^2}{\partial\phi^2} + \frac{1}{1-\eta^2}\frac{\partial^2}{\partial\phi^2}\right]$$

$$\nabla = \mathbf{e}_\xi \frac{2}{R}\sqrt{\frac{\xi^2-\eta^2}{\xi^2-1}}\frac{\partial}{\partial\xi} + \mathbf{e}_\eta \frac{2}{R}\sqrt{\frac{\xi^2-\eta^2}{1-\eta^2}}\frac{\partial}{\partial\eta} + \mathbf{e}_\phi \frac{2}{R}\frac{1}{\sqrt{(\xi^2-1)(1-\eta^2)}}\frac{\partial}{\partial\phi} \tag{11}$$

If the distance from the molecule is large, ξ is large, and we can then approximate $\mathbf{r} = (\sqrt{1-\eta^2}\cos\phi, \sqrt{1-\eta^2}\sin\phi, \eta)R\xi/2$. Hence, it becomes clear that $\eta \approx \cos\theta$ in spherical coordinate systems, and $\xi \approx 2r/R$.

We want to solve

$$(-\nabla^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{R})\psi = E\psi$$

We look for the solution with the following separable ansatz

$$\psi(\xi,\eta,\phi) = (\xi^2-1)^{m/2}X(\xi)(1-\eta^2)^{m/2}Y(\eta)e^{\pm im\phi} \tag{12}$$

Inserting the ansatz into diff. equation leads to

$$\frac{4}{R^2(\xi^2-\eta^2)}\left[2(m+1)\xi X'(\xi)+(\xi^2-1)X''(\xi)\right]Y+$$
$$\frac{4}{R^2(\xi^2-\eta^2)}\left[-2(m+1)\eta Y'(\eta)+(1-\eta^2)Y''(\eta)\right]X+$$
$$\left(\frac{4}{R(\xi+\eta)}+\frac{4}{R(\xi-\eta)}+(E-\frac{2}{R})\right)XY=0 \qquad (13)$$

Here we used $X'(\xi)\equiv dX/d\xi$ and $X''(\xi)\equiv d^2X/d\xi^2$.

Differential equation can be set into a separable form

$$\frac{1}{X}\left[2(m+1)\xi X'(\xi)+(\xi^2-1)X''(\xi)\right]+$$
$$\frac{1}{Y}\left[-2(m+1)\eta Y'(\eta)+(1-\eta^2)Y''(\eta)\right]+$$
$$\left(2R\xi-(\xi^2-\eta^2)p^2\right)=0 \qquad (14)$$

where we introduced parameter p:

$$p^2=-\frac{R^2}{4}(E-\frac{2}{R})$$

.

The final form of the normal differential equations is

$$(\xi^2-1)X''(\xi)+2(m+1)\xi X'(\xi)+(-p^2\xi^2+A+2R\xi)X=0 \quad (15)$$

$$-(1-\eta^2)Y''(\eta)+2(m+1)\eta Y'(\eta)+(-p^2\eta^2+A)Y=0 \quad (16)$$

The boundary conditions are

$$\psi(\xi\to\infty)=0 \quad (17)$$

$$\nabla\psi<\infty \quad (18)$$

The second diff.equation has even-odd symmetry. This is due to the fact that $\eta\to-\eta$ leaves equation unchanged. Hence, solution has to be even ($Y(-\eta)=Y(\eta)$) or odd ($Y(-\eta)=-Y(\eta)$). The standard name for odd (even) functions is "gerade" ("ungerade").

The boundary condition for ungerade functions is $Y'(0)=0$ and for gerade is $Y(0)=0$. The second boundary condition is arbitrary, but we will choose $Y(1)=1$ for simplicity. We will later normalize the function.

At large distance the wave function has to vanish, hence $X(\xi\to\infty)=0$. For the kinetic energy to be finite everywhere, a quick look at the ∇ operator shows that $X'(\xi=1)=0$.

We hence have the following boundary conditions

$$X(\xi \to \infty) = 0 \tag{19}$$

$$X'(\xi = 1) = 0 \tag{20}$$

$$Y(\eta = 1) = 1 \tag{21}$$

$$Y(\eta = 0) = 0 \quad or \quad Y'(\eta = 0) = 0 \tag{22}$$

We will use double-shooting method to find p and A for the bound states.

We will solve diff. equation $Y(\eta)$ to get connection between p and A, i.e., $A(p)$. We will solve $X(\xi)$ to pick p that correspdonds to a bounded state.

We need a good guess for parameters p and A. At small distance (equivalent to He^+ ion) these parameters are

$$\lim_{R\to 0} A = -l(l+1) \tag{23}$$

$$\lim_{R\to 0} p = 0 \tag{24}$$

where l is angular momentum eigenvalue of He ion.

When atoms are far apart, $E = -1, -1/4, ...$ and hence $p = R/2, R/4, ...$ The

ground state will have largest p, which will be slighly larger than $R/2$ because delocalization of electron leads to lower energy when ions get close together. We will look for possible solutions in the interval $p \in [R/2 + 0.6, ...R/4]$. We notice that p can be smaller (but positive) for high-excited states.

At finite separation, A grows and is largest for the groundstate. For small p, $A(p^2)$ has an expansion in power series, which looks like $A(p^2) = -l(l+1) + p^2/3 + ...$ A good interval for values of A is $A \in [p^2/2 + p^3/2 - l(l+1), ..., -l(l+1)]$.

Below we sketch algorithm

- Create a good mesh for solving diff. equation in variables ξ and η. A good choice for η is linear mesh (with 50 points). (Be careful and do not put point at $|\eta| = 1$, but rather at $|\eta| = 1 - \delta$ with $\delta \approx 10^{-7}$. For ξ we will use logarithmic mesh $\xi \in [1 + \delta, \xi_{max}]$, where $\xi_{max} \approx 30/p$. A mesh with 200 point is sufficient.
- First we will find value of A at constant p (i.e., $A(p)$), which satisfies diff. equation $Y(\eta)$. This will be achieved by the shooting method: parameter A will be varied (on linear mesh) between $p^2/2 + p^3/12$ and $-l_{max}(l_{max}+1)$ (we will use $l_{max} = 2$ in this expression, and we will use 10 points only). Once a change of sign in $Y(0)$ [$Y'(0)$] is detected for ungerade [gerade] state, we use root finding routine to

determine $A(p)$.

For numeric integration of $Y(\eta)$ we need initial conditions. You can use $Y(1) = 1$ and $Y'(1) = (p^2 - A)/(2(m+1))$. This is because

$$Y''(\eta) = \frac{2(m+1)\eta Y'(\eta) + (A - p^2\eta^2)Y}{1-\eta^2} \tag{25}$$

hence $Y''(1)$ is finite only if $Y'(1) = -(A-p^2)/(2m+1)$.

- Once $A(p)$ is determined, we integrate equation for $X(\xi)$ to see if current value of p is such that satisfies the boundary condistion. We will start integrating from $\xi = \infty$ down to $\xi = 1$ and we will look for function with $X'(\xi = 1) = 0$. We will need to vary p to find such function. This will be done in the outside loop.

- The outside loop iterates through a set of linearly distributed values for parameter p between $R/2 + 0.6$ and $R/4$. When the above described shooting methods detects a sign-change in $X'(\xi = 1)$, it calls root-finding routine to determine p to high accuracy. The bound states are saved in a list.

- Once parameters A and p are determined, we recompute $Y(\eta)$ and $X(\xi)$. We create an interpolating object for $(\xi^2 - 1)^{m/2}X(xi)$ and $(1-\eta^2)^{m/2}Y(\eta)$, such that

$\psi(\xi, \eta, \phi)$ can be calculated at any point.

- For ploting the 2D density plot of the wave function, we generate a regular mesh of cartesian $[x, z]$ points. We compute prolate coordinates $[\xi, \eta, \phi]$ from cartesian vector $[x, y, z]$ from

$$\widetilde{r} = \frac{\sqrt{x^2 + y^2 + z^2}}{R/2} \tag{26}$$

$$\widetilde{z} = \frac{z}{R/2} \tag{27}$$

$$sq = \sqrt{(1 + \widetilde{r}^2)^2 - 4\widetilde{z}^2} \tag{28}$$

$$\xi = \sqrt{(1 + \widetilde{r}^2 + sq)/2} \tag{29}$$

$$\eta = \sqrt{(1 + \widetilde{r}^2 - sq)/2}\ \text{sign}(z) \tag{30}$$

$$\phi = \arctan(y, x) \tag{31}$$

The transformation from prolate to cartesian coordinates is simpler

$$\widetilde{\rho} = \sqrt{\xi^2 - 1}\sqrt{1 - \eta^2} \tag{32}$$

$$(x, y, z) = (\widetilde{\rho}\cos\phi, \widetilde{\rho}\sin\phi, \xi\eta)R/2 \tag{33}$$

We evaluate $\psi(\mathrm{r})$ and plot a density plot.

We choose $R = 2$, which is very close to equilibrium distance of H_2^+. We first evaluate a few lowest energy gerade states at $m = 0$:

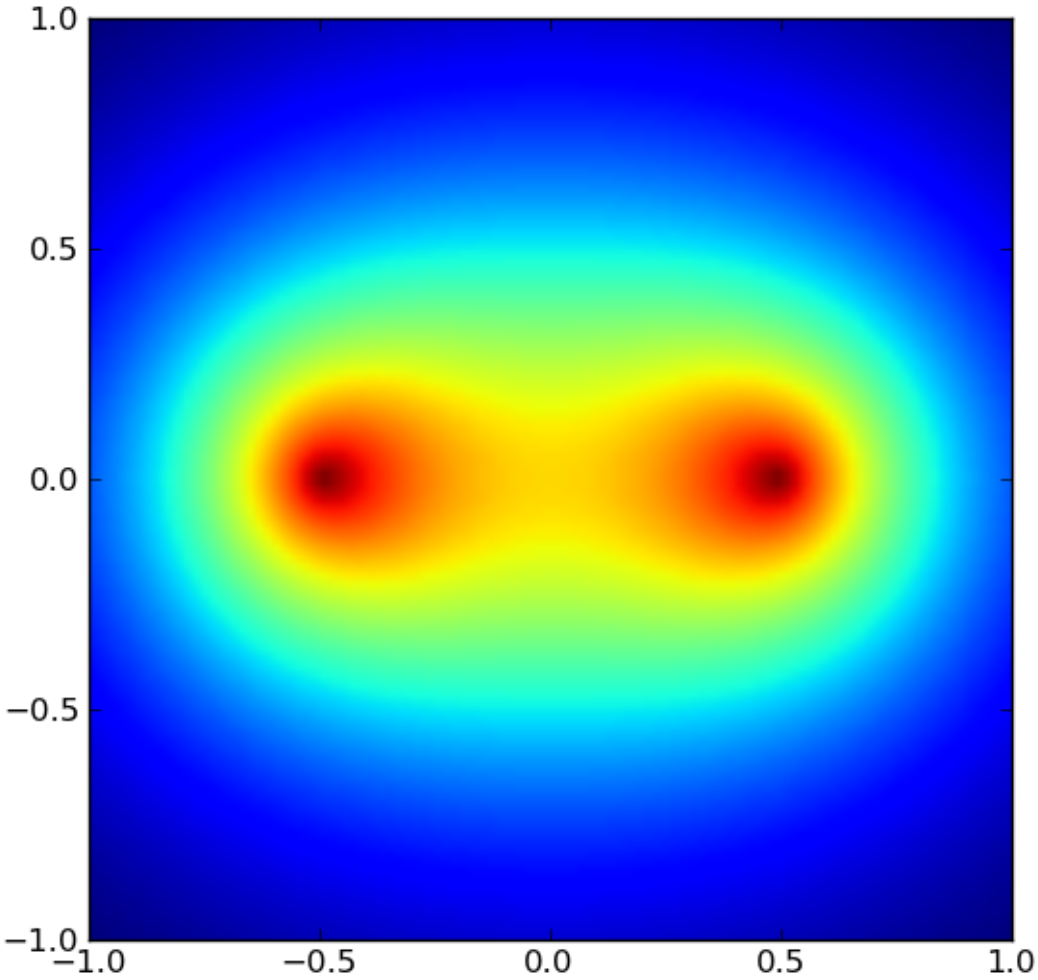
$$1\sigma_g : (p, A, E) = (1.48501486965, 0.811729880903, -1.20526916309)$$
$$2\sigma_g : (p, A, E) = (0.849562360518, 0.248475561369, 0.278243795591)$$
$$3\sigma_g : (p, A, E) = (0.596209803892, 0.120381543784, 0.644533869744)$$

and ungerade states at $m = 0$:

$$1\sigma_u : (p, A, E) = (1.15545267065, -1.18688803994, -0.33507087412)$$
$$2\sigma_u : (p, A, E) = (0.714744398137, -1.691702919, 0.489140445332)$$
$$3\sigma_u : (p, A, E) = (0.524110147939, -1.83466895941, 0.725308552828)$$

and finally $m = 1$ gives:

$$1\pi_g : (p, A, E) = (0.926036766069, 0.174948548517, 0.142455907889)$$
$$1\pi_u : (p, A, E) = (0.673353143116, -3.80488326247, 0.546595544656)$$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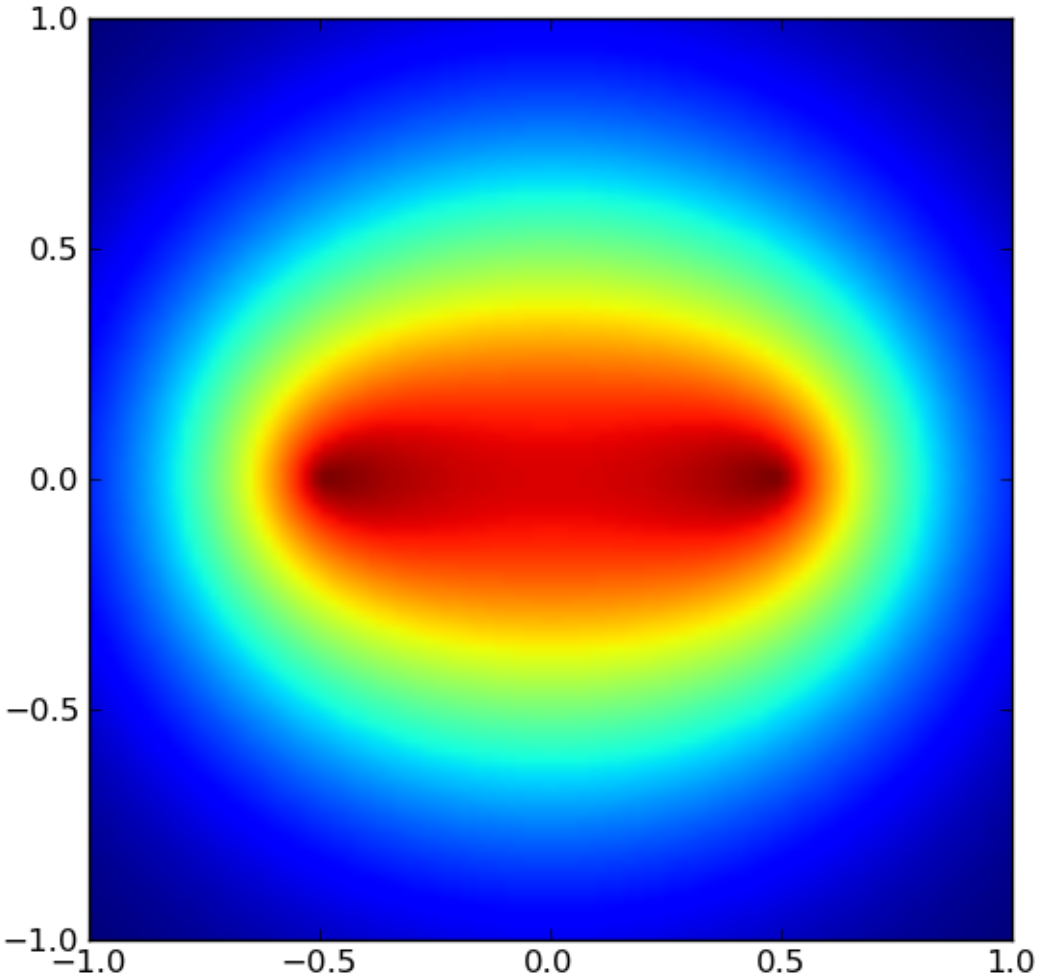
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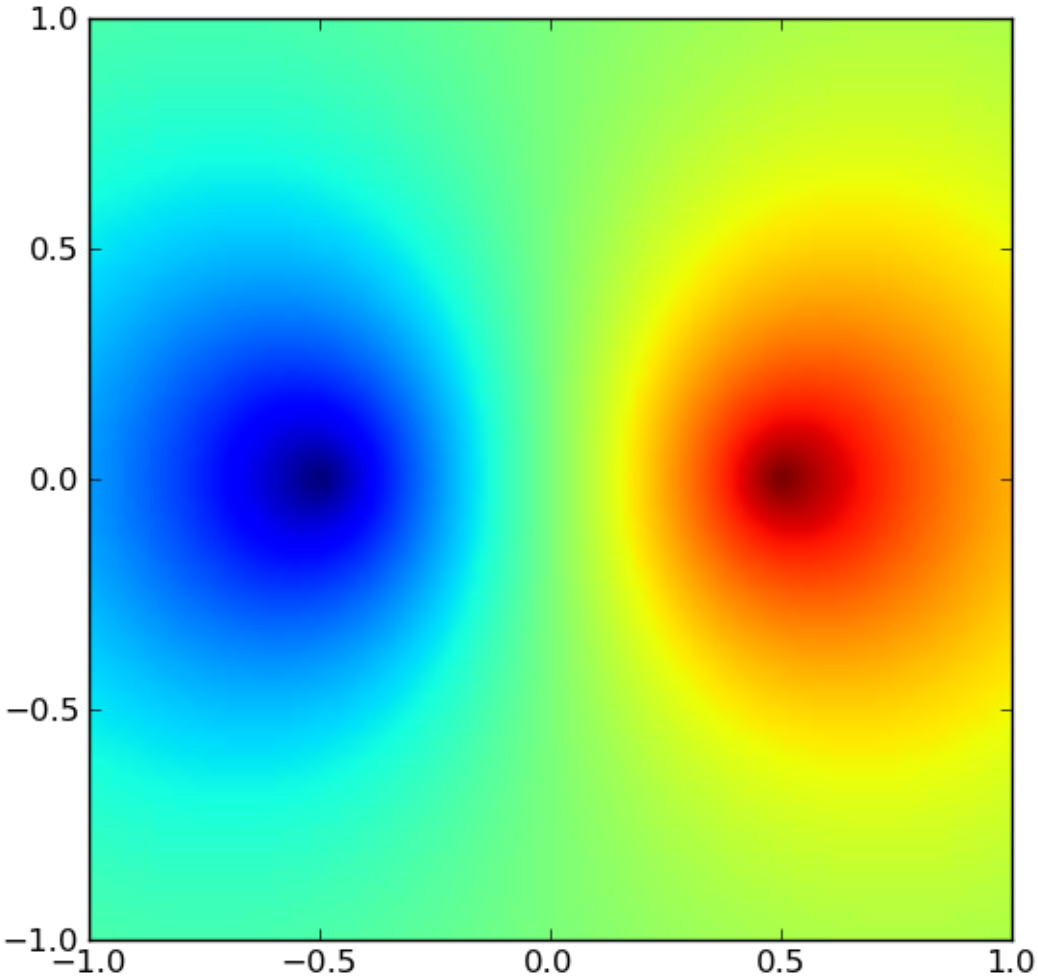
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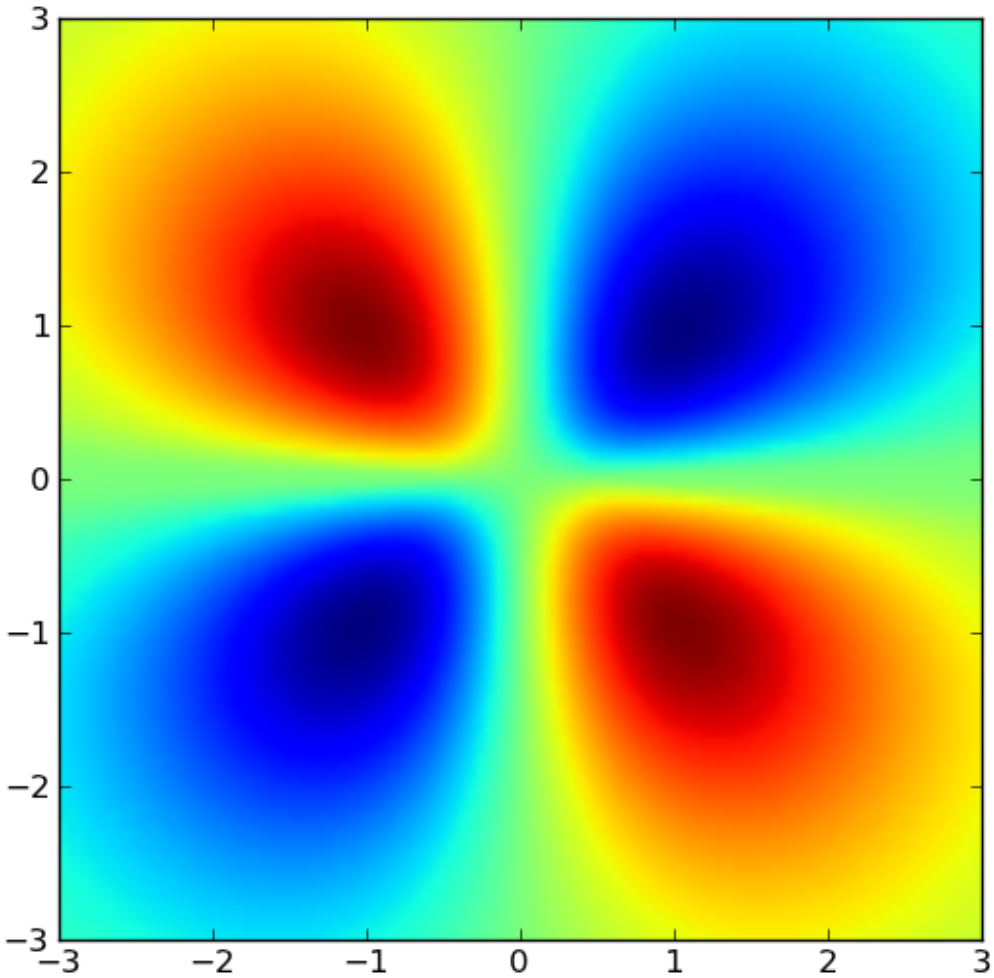
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