Chem 195: Problem Set 3

Michael Stephen Chen

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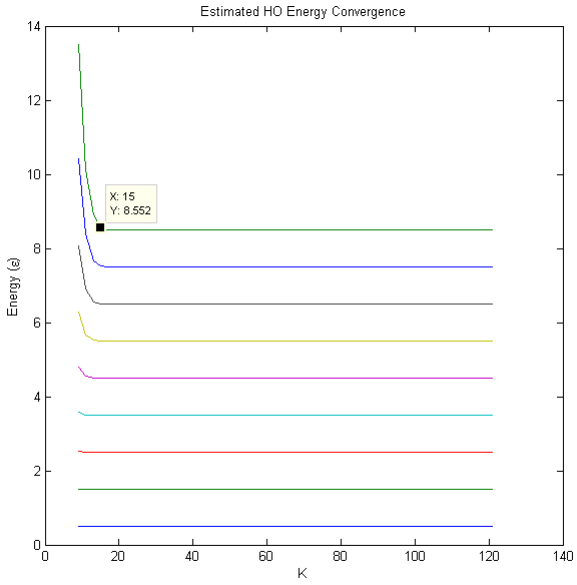
Problem 1

i. See *ho.m* for all my added comments

ii. The following are the calculatedenergies for the 9 lowest energy levels. To reprodue these results, run the first section of *HOConverge1D.m*

$Level$	$Energy(\epsilon)$
0	0.5001
1	1.5021
2	2.5176
3	3.5944
4	4.8016
5	6.2846
6	8.0551
7	10.4124
8	13.4974

iii. Below is a plot showing the convergence of energy levels with increasing number of basis functions K. Qualitatively, it appears that convergence is achieved for the lowest nine levels around $K = 15$



Problem 2

i.

$$\begin{aligned}
H\psi &= \left[-\frac{1}{2}\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}\right)+\frac{1}{2}(x^2+y^2)\right](\psi_x\psi_y) \\
&= \frac{1}{2}\left(-\frac{d^2}{dx^2}+x^2\right)(\psi_x\psi_y)+\frac{1}{2}\left(-\frac{d^2}{dy^2}+y^2\right)(\psi_x\psi_y) \\
&= \psi_y\left[\frac{1}{2}\left(-\frac{d^2}{dx^2}+x^2\right)\psi_x\right]+\psi_x\left[\frac{1}{2}\left(-\frac{d^2}{dy^2}+y^2\right)\psi_y\right] \\
&= \psi_y E_x\psi_x+\psi_x E_y\psi_y \\
&= (E_x+E_y)\,\psi_x\psi_y
\end{aligned}$$

ii. The following is the equation for the energy of the 2D-HO given n_x and n_y where $n_x, n_y \in \mathbb{N}$

$$\begin{aligned}
E &= E_x+E_y \\
&= (n_x+1/2)+(n_y+1/2) \\
&= n_x+n_y+1
\end{aligned}$$

An enumeration of the first couple energy states $n = n_x + n_y$ is presented below. In general the number of degeneracies is equivalent to $n+1$

n	n_x	n_y	$Energy(\epsilon)$
0	0	0	1
1	1	0	2
	0	1	
2	1	1	3
	2	0	
	0	2	

Problem 3

Below is the code from *harmOsc2DEnergies.m*

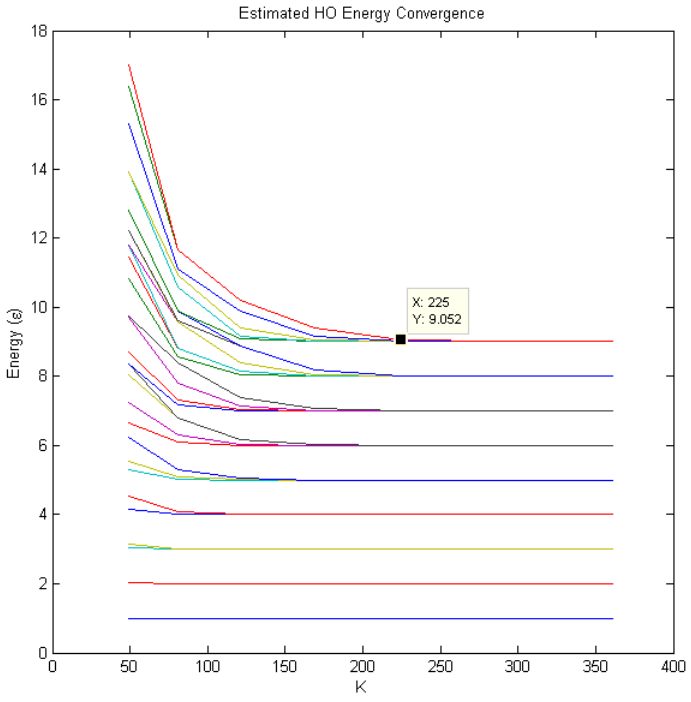
```
function [energ, wf] = harmOsc2DEnergies(K, alpha, space)

    n = (sqrt(K) - 1) / 2;

    % Problem 3 part (i), enumerating the bases
    k = -n*space:space:n*space;
    k_sqr = zeros(length(k)^2, 2);
    i = 1;
    for x = -n*space:space:n*space
        for y = -n*space:space:n*space
            k_sqr(i, :) = [x, y];
            i = i + 1;
        end
    end

    % Problem 3 part(ii), calculating the matrix elements
    num_pts = length(k_sqr);
    S = zeros(num_pts, num_pts);
    H = zeros(num_pts, num_pts);
    for ia = 1:num_pts
        xA = k_sqr(ia, 1);
        yA = k_sqr(ia, 2);
        for ib = 1:num_pts
            xB = k_sqr(ib, 1);
            yB = k_sqr(ib, 2);

            x_diff2 = (xA - xB)^2;
            y_diff2 = (yA - yB)^2;
            xP2 = ((xA + xB) / 2)^2;
            yP2 = ((yA + yB) / 2)^2;

            S(ia, ib) = (pi/ 2*alpha) * exp(-alpha*x_diff2/2 - alpha*y_diff2/2);
            H(ia, ib) = (S(ia,ib)/2) * ...
                (2*alpha - alpha^2*(x_diff2 + y_diff2) + 1/(2*alpha) + xP2 + yP2);
        end
    end

    % Problem 3 part(iii), solving for eigenvalues/eigenfns
    [wf, D] = eig(S\H);
    energ = diag(D);
    for i = 1:size(wf, 2)
        c = wf(:, i);
        norm = 1/sqrt(c'*S*c);
        wf(:, i) = c * norm;
    end

end
```

Problem 4

i. Below are the calculated energies for the 45 lowest energy eigenstatess for $K = 49$ basis fns. The results can be reproduced by running the first section of *HOConverge2D.m*. The result for the ground state and the first excited statess are fairly close to the theoretical values of 1 and 2, respectively. Also we can see the degeneracy of the first excited state. However with increassing energy levels the calculated value deviate more and more.

$index$	$Energy(\epsilon)$
1	1.0036
2	2.0291
3	2.0291
4	3.0545
5	3.1434
6	3.1434
7	4.1688
8	4.1688
9	4.5276
10	4.5276
11	5.2831
12	5.5531
13	5.5531
14	6.2278
15	6.2278
16	6.6674
17	6.6674
18	7.2532
19	7.2532
20	8.0516
21	8.3675
22	8.3675
23	8.6903
24	8.6903
25	9.7158
26	9.7158
27	9.7518
28	9.7518
29	10.8301
30	10.8301
31	11.4519
32	11.7807
33	11.7807
34	12.2143
35	12.2143
36	12.8061
37	12.8061
38	13.9145
39	13.9145
40	13.9205
41	13.9205
42	15.3047
43	15.3047
44	16.3770
45	17.0049

ii. To reproduce the figure below, please run the second section of *HOConverge2D.m*. It appears as though $K = 225$ basis are necessary for convergence of the first 9 energy levels for the 2D HO.

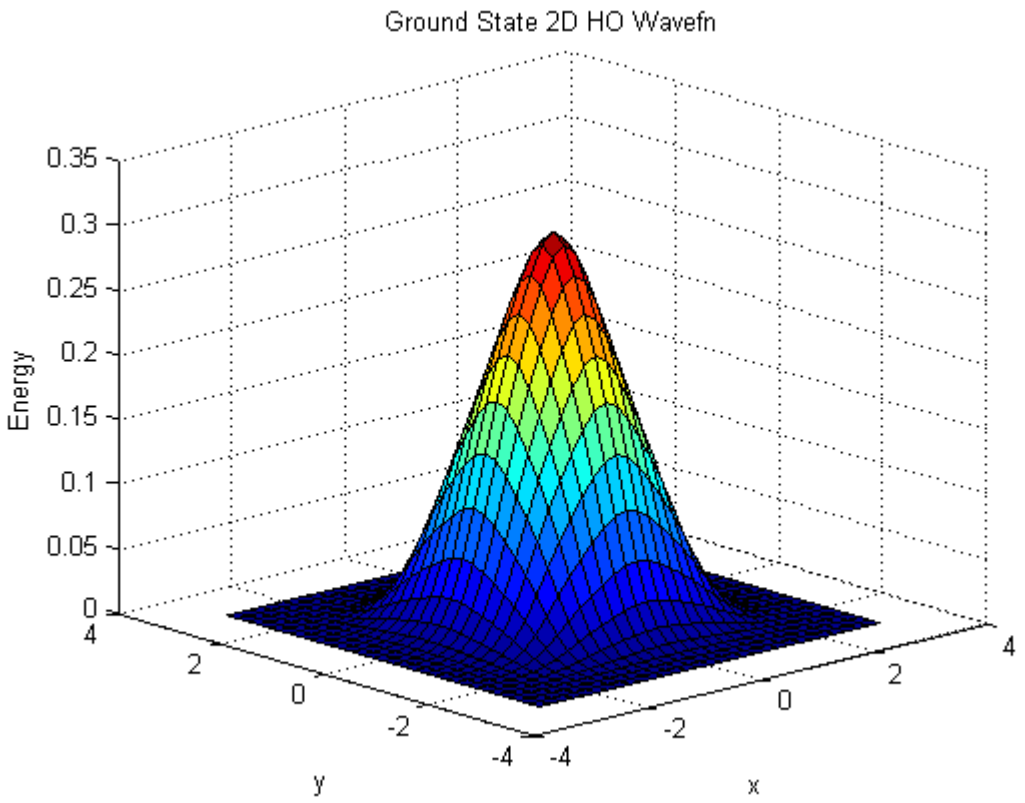


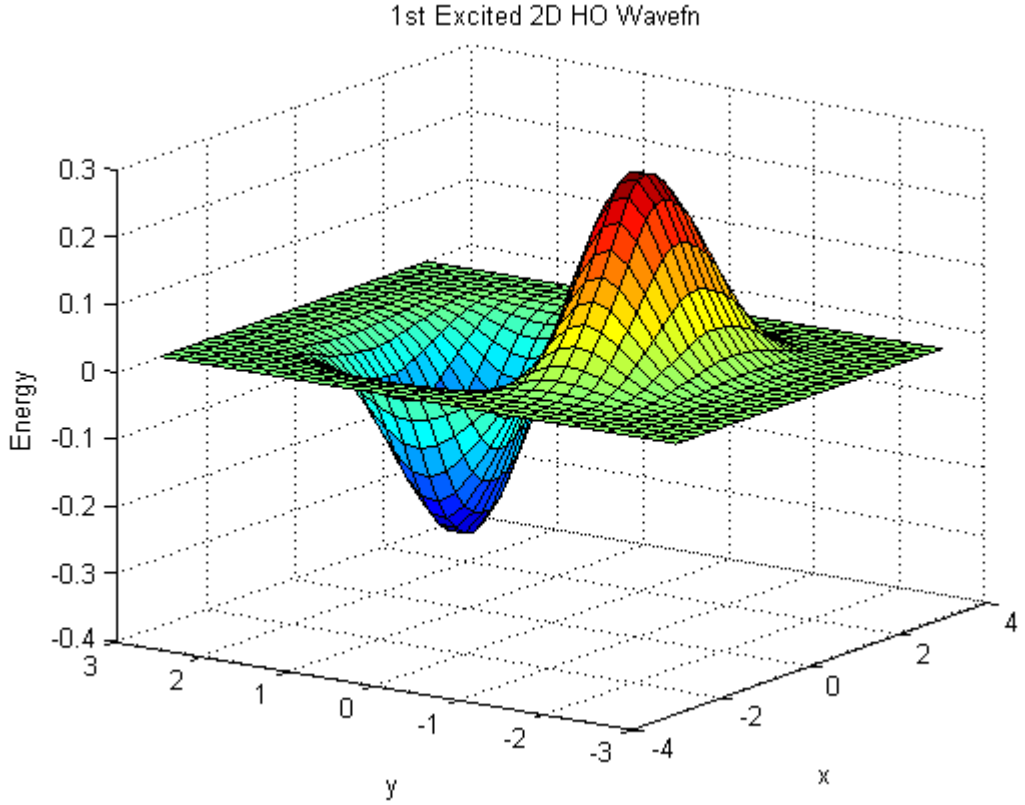
iii. Given that for the 1D HO we needed around 15 basis fns and we needed apprximately $15^2 = 225$ basis fns for a 2D HO, we would probably need $15^3 = 3375$ basis fns for the first 9 energy levels to converge for a 3D HO. So in general the dimensionality of the wavefn $\psi(x_1, x_2, ..., x_N)$ will require roughly c^N basis functions, where c is some constant intrinsic to the problem at hand, or in another words the number of basis functions scale exponentially with the dimensionality of the wavefn/equation we are solving for.

iv. Therefore with N-electron problems in 3D where we have 3N coordinates, the computational expense should be $O(c^{3N})$. So the computational expense grows very quickly with increasing number of electrons, making such calculationss slow/infeasible for large N.

Problem 5

The wavefunctions were calculated using $K = 25$ basis sets. To reproduce the following, run the file *HOWavefnPlot.m*


Ground State 2D HO Wavefn
Energy
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
4
2
0
-2
-4
y
-4
-2
0
2
4
x


1st Excited 2D HO Wavefn
Energy
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
3
2
1
0
-1
-2
-3
y
-4
-2
0
2
4
x