CHM452: Problem Set 3

Xinxian Chen*

April 13, 2020

Let $\mathrm{i} = \sqrt{-1}$, $o(\cdot)$ and $O(\cdot)$ are little-o and big-O notations, respectively, and $\mathbb{N}$ is the set of natural numbers ($\mathbb{N} = \{0,\ 1,\ 2,\ 3,\ \ldots\}$) and $\mathbb{N}_+ = \mathbb{N} \setminus \{0\}$

Code available at `https://github.com/vINyLogY/QD-hw3`.

1. Set $\hbar = 1$.

(i) Analytically, when $x_0 = 0$ and $p_0 = 0$,

$$\langle x^2 \rangle = \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \mathrm{d}x\, x^2 e^{-\alpha x^2} = \left(\frac{\alpha}{\pi}\frac{\pi}{4\alpha^3}\right)^{1/2} = \frac{1}{2\alpha}, \langle x \rangle = \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \mathrm{d}x\, x e^{-\alpha x^2} = 0.$$

When $\alpha = 1$, $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = 1/\sqrt{2} \approx 0.70710678$.

Use the grid basis in the range $[-20,\ 20]$ and the number of grid points be 1024, and results are:

norm: 1.00000000; $\langle x \rangle$: 0.00000000; and Δx: 0.70710678.

The wavefunction is plotted in Figure 1.

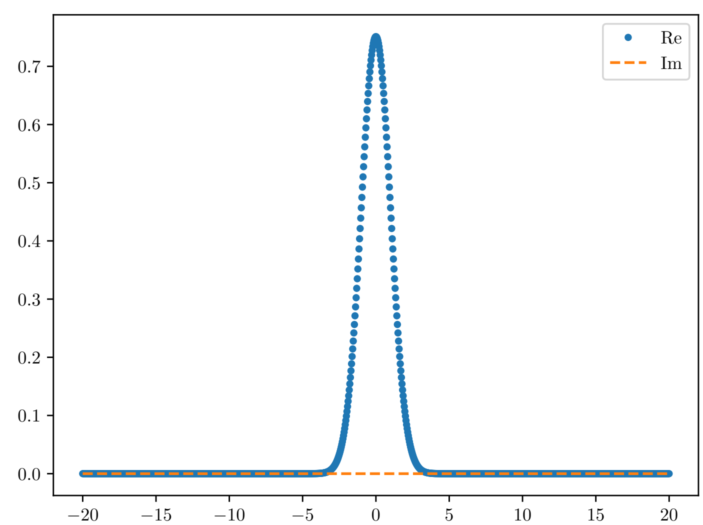


Figure 1

(ii) Analytically, when $x_0 = 0$ and $p_0 = 0$, the fourier transformation gives

$$\begin{aligned}\Psi_0(p) &= \frac{1}{\sqrt{2\pi}} \int \mathrm{d}x\, e^{-\mathrm{i}px} \Psi_0(x) = \frac{1}{\sqrt{2\pi}} \left(\frac{\alpha}{\pi}\right)^{1/4} \int \mathrm{d}x\, e^{-\mathrm{i}px - \alpha x^2/2} \\ &= \frac{1}{\sqrt{\alpha}} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-p^2/(2\alpha)},\end{aligned}$$

*Email: xchen106@ur.rochester.edu

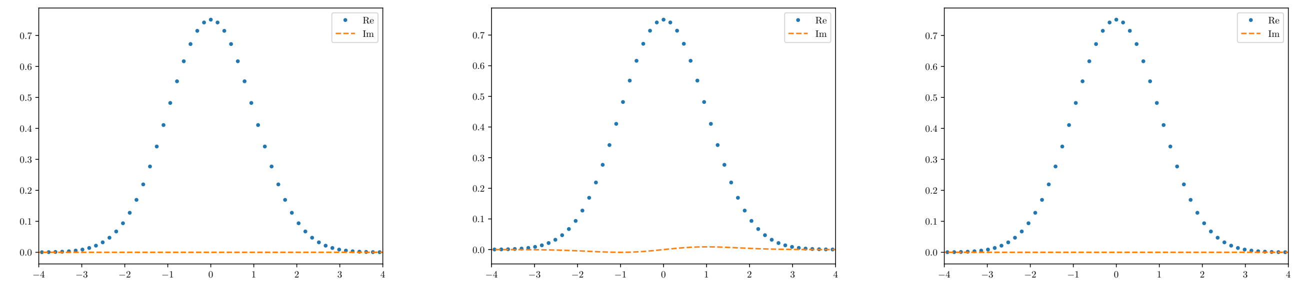
and when $\alpha = 1$,

$$\Psi_0(p) = \left(\frac{1}{\pi}\right)^{1/4} e^{-p^2/2},$$

Hence, follow the same procedure we will find that $\langle p \rangle = 0$, $\left\langle p^2 \right\rangle = 1/2$ and $\Delta p = 1/\sqrt{2} \approx 0.70710678$.
Use the grid basis in the range $[-20,\ 20]$ and the number of grid points be 1024 and 1025, and results are:

1024 grid points: norm: 1.00000000; $\langle p \rangle$: 0.00000000; and Δp: 0.70849123;
1024 grid points: norm: 1.00000000; $\langle p \rangle$: 0.00000000; and Δp: 0.70848987;
1025 grid points: norm: 1.00000000; $\langle p \rangle$: 0.00000000; and Δp: 0.70848852.

The wavefunction is plotted in Figure 2.



1023 grid points   1024 grid points   1025 grid points

Figure 2

Note that the relevant errors of Δp are larger than the ones of Δx, and the when the number of grid points is odd the results are more accurate than the case that the number of grid points is similar but is even. This can be also justified the imaginary part of the wavefunction in momentum space.

(iii) With 1024 gird points, the answer is

Potential: 0.25000000; Kinetic: 0.25097895; Total = 0.50097895.

With $2^{20} = 1048576$ gird points, the answer is

Potential: 0.25000000; Kinetic: 0.25000095; Total: 0.50000095.

Note that the analytical expectation of the total energy is 0.5.

2. (i) Use $2^{12} = 4096$ grid points uniformly spanned on $[-20,\ 20]$. Results plotted in Figure 3.

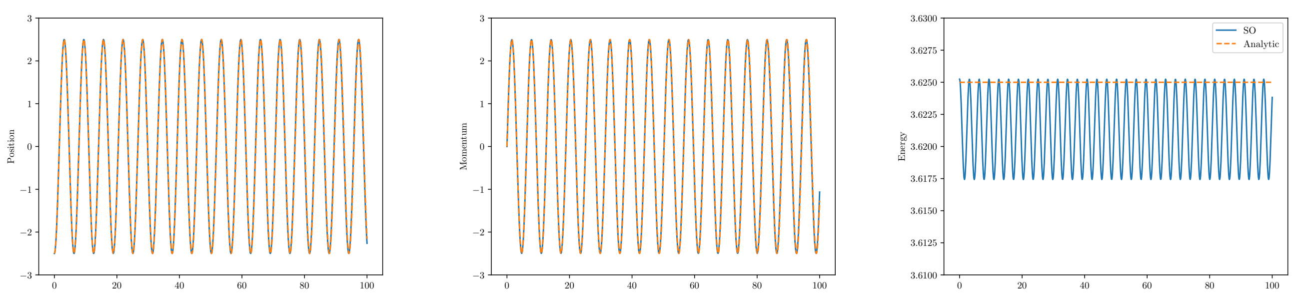


Figure 3

The movie is showed in `q2-1.mp4`.

(ii) Still use $2^{12} = 4096$ grid points uniformly spanned on $[-20,\ 20]$. Results plotted in Figure 4.

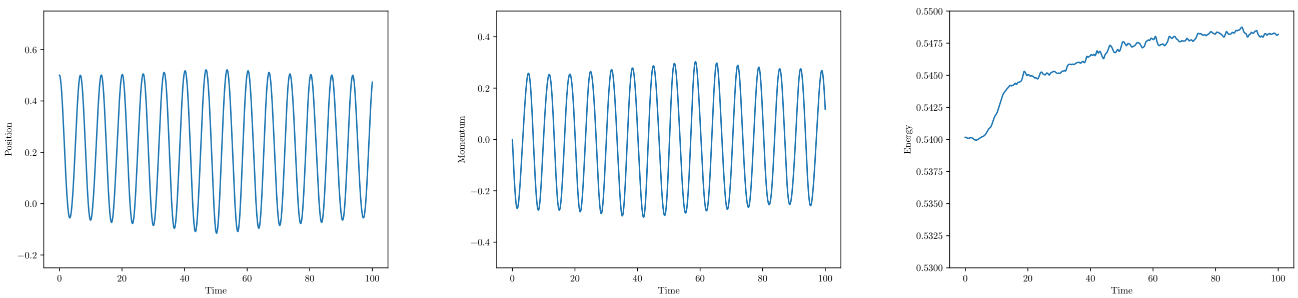


Figure 4

The movie is showed in `q2-2.mp4`.

(iii) The energy of the ground state calculated by (Sine-)DVR (spanned on $[-20,\ 20]$ using 1024 basis) is 0.49218750 a. u., while imaginary time propagation SO (using grid basis spanned on $[-20,\ 20]$ with 4096 grid points, time step is $-0.1\mathrm{i}$) gives 0.49242469 a. u.. The wavefunction of the ground state is plotted in Figure 5.

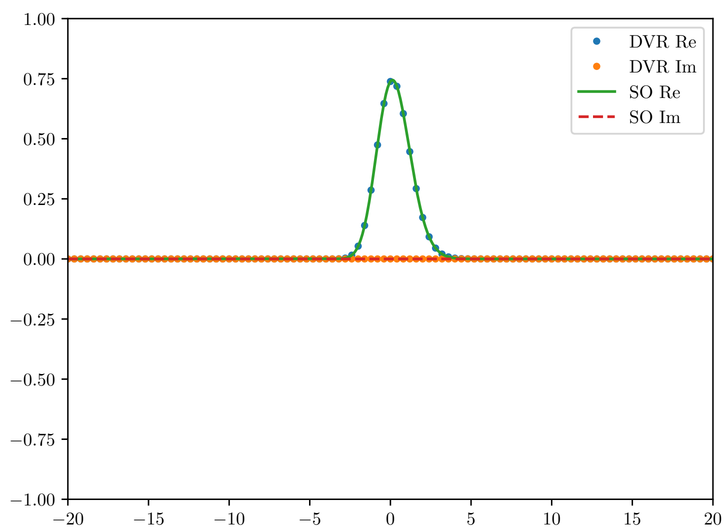


Figure 5

(iv) Use $2^{12} = 4096$ grid points uniformly spanned on $[-20,\ 20]$. See `q2-4.mp4`. Note that the potential function used in the propagator $\tilde{V}(x) = V(x) - V_a(x)$ in order to absorb the wavefunction moved out from $[-10,\ 10]$.

3. (i) Note that $\hat{V}$ matrix is hermitian. Let

$$\det\left(\lambda - \hat{V}\right) = \det\left(\lambda - \begin{pmatrix} V_1 & V_{12} \\ V_{21} & V_2 \end{pmatrix}\right) = 0,$$

that is,

$$\lambda^2 - (V_1 + V_2)\lambda + V_1 V_2 - |V_{21}|^2 = 0,$$

$$\lambda = \frac{(V_1 + V_2) \pm \sqrt{(V_1 + V_2)^2 - 4V_1V_2 + 4|V_{21}|^2}}{2}.$$

Hence, $\lambda_1 = \frac{1}{2}\Big((V_1+V_2)+\sqrt{D}\Big)$, $\lambda_2 = \frac{1}{2}\Big((V_1+V_2)-\sqrt{D}\Big)$, where $D = 4|V_{21}|^2 + (V_1-V_2)^2$. Therefore, there are unitary transformation $\hat{U}$ such that

$$\hat{V} = \begin{pmatrix} V_1 & V_{12} \\ V_{21} & V_2 \end{pmatrix} = \frac{1}{2}\hat{U}\begin{pmatrix} (V_1+V_2)+\sqrt{D} & \\ & (V_1+V_2)-\sqrt{D} \end{pmatrix}\hat{U}^\dagger.$$

Hence,

$$\begin{aligned}
\exp\left[-\frac{\mathrm{i}\Delta t}{\hbar}\begin{pmatrix} V_1 & V_{12} \\ V_{21} & V_2 \end{pmatrix}\right] &= \hat{U}\begin{pmatrix} \exp\left[-\frac{\mathrm{i}\Delta t}{2\hbar}\Big((V_1+V_2)+\sqrt{D}\Big)\right] & \\ & \exp\left[-\frac{\mathrm{i}\Delta t}{2\hbar}\Big((V_1+V_2)-\sqrt{D}\Big)\right] \end{pmatrix}\hat{U}^\dagger \\
&= \exp\left[-\frac{\mathrm{i}\Delta t}{2\hbar}(V_1+V_2)\right]\hat{U}\begin{pmatrix} \exp\left[-\frac{\mathrm{i}\Delta t}{2\hbar}\sqrt{D}\right] & \\ & \exp\left[\frac{\mathrm{i}\Delta t}{2\hbar}\sqrt{D}\right] \end{pmatrix}\hat{U}^\dagger.
\end{aligned}$$

Let $\theta = \frac{\Delta t}{2\hbar}\sqrt{D}$, then

$$\begin{aligned}
\exp\left[-\frac{\mathrm{i}\Delta t}{\hbar}\begin{pmatrix} V_1 & V_{12} \\ V_{21} & V_2 \end{pmatrix}\right] &= \exp\left[-\frac{\mathrm{i}\Delta t}{2\hbar}(V_1+V_2)\right]\hat{U}\begin{pmatrix} \cos\theta - \mathrm{i}\sin\theta & \\ & \cos\theta + \mathrm{i}\sin\theta \end{pmatrix}U^\dagger \\
&= \exp\left[-\frac{\mathrm{i}\Delta t}{2\hbar}(V_1+V_2)\right]\left[\cos\theta + \mathrm{i}\sin\theta\Big(u_2u_2^\dagger - u_1u_1^\dagger\Big)\right],
\end{aligned}$$

where

$$\begin{pmatrix} V_1 & V_{12} \\ V_{21} & V_2 \end{pmatrix}u_i = \lambda_i u_i, \quad i = 1,\ 2.$$

When $i = 1$, solve the null space of $\lambda_1 - \hat{V}$ we have the unnormalized $\tilde{u}_1 = (V_1 - V_2 + \sqrt{D},\ 2V_{21})^\mathsf{T}$, and hence,

$$u_1u_1^\dagger = \frac{\tilde{u}_1\tilde{u}_1^\dagger}{\tilde{u}_1^\dagger\tilde{u}_1} = \frac{1}{2\sqrt{D}(V_1-V_2+\sqrt{D})}\begin{pmatrix} (V_1-V_2)^2 + 2\sqrt{D}(V_1-V_2) & 2V_{12}\Big(V_1-V_2+\sqrt{D}\Big) \\ 2V_{21}\Big(V_1-V_2+\sqrt{D}\Big) & 4|V_{12}|^2 \end{pmatrix}.$$

Similarly, $\tilde{u}_2 = (-2V_{12},\ V_1 - V_2 + \sqrt{D})^\mathsf{T}$, and

$$u_2u_2^\dagger = \frac{1}{2\sqrt{D}(V_1-V_2+\sqrt{D})}\begin{pmatrix} 4|V_{12}|^2 & -2V_{12}\Big(V_1-V_2+\sqrt{D}\Big) \\ -2V_{21}\Big(V_1-V_2+\sqrt{D}\Big) & (V_1-V_2)^2 + 2\sqrt{D}(V_1-V_2) \end{pmatrix}.$$

Hence,

$$\begin{aligned}
\exp\left[-\frac{\mathrm{i}\Delta t}{\hbar}\begin{pmatrix} V_1 & V_{12} \\ V_{21} & V_2 \end{pmatrix}\right] &= \exp\left[-\frac{\mathrm{i}\Delta t}{2\hbar}(V_1+V_2)\right]\left[\cos\theta + \mathrm{i}\sin\theta\Big(u_2u_2^\dagger - u_1u_1^\dagger\Big)\right] \\
&= \exp\left[-\frac{\mathrm{i}\Delta t}{2\hbar}(V_1+V_2)\right]\left[\cos\theta + \mathrm{i}\frac{\sin\theta}{2\sqrt{D}(V_1-V_2+\sqrt{D})}\cdot\right. \\
&\quad \left.\begin{pmatrix} 4|V_{12}|^2 - (V_1-V_2)^2 - 2\sqrt{D}(V_1-V_2) & -4V_{12}\Big(V_1-V_2+\sqrt{D}\Big) \\ -4V_{21}\Big(V_1-V_2+\sqrt{D}\Big) & (V_1-V_2)^2 + 2\sqrt{D}(V_1-V_2) - 4|V_{12}|^2 \end{pmatrix}\right] \\
&= \exp\left[-\frac{\mathrm{i}\Delta t}{2\hbar}(V_1+V_2)\right]\left[\cos\theta + \mathrm{i}\frac{\sin\theta}{\sqrt{D}}\begin{pmatrix} V_2 - V_1 & -2V_{12} \\ -2V_{21} & V_1 - V_2 \end{pmatrix}\right].
\end{aligned}$$

(ii) Use 1024 grid points, other parameters are the given values in the Problem Set. Results plotted in Figure 6. Note that the energy is almost a constant of 1.43727 eV with the error of 10^{-6} scale. The movie is showed in `q3-2.mp4`.

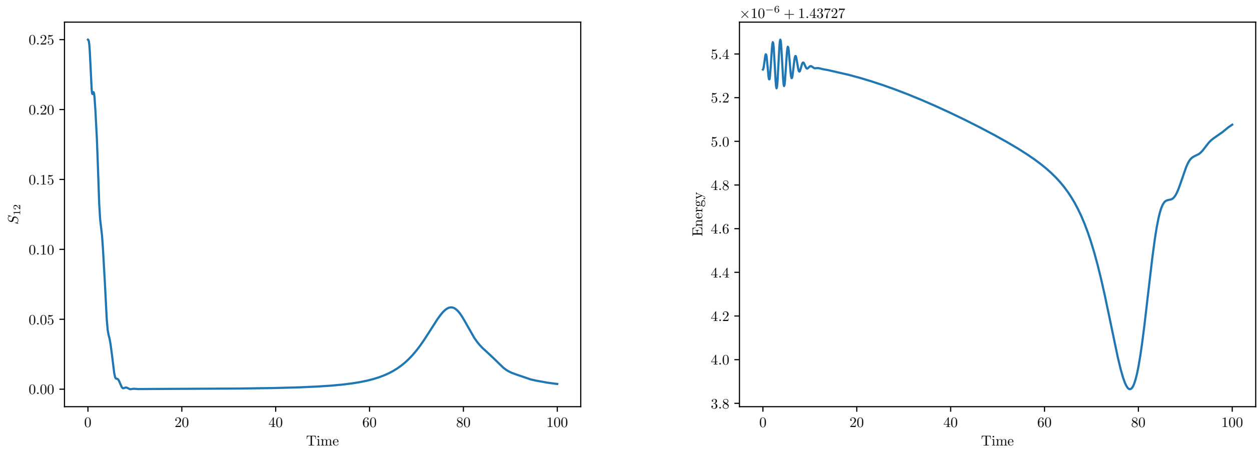


Figure 6

The wavepacket on $|2\rangle$ gradually moves to the minimum points of the potential surface of $|2\rangle$ and then hops back to $|1\rangle$.

(iii) Use 1024 grid points, other parameters are the given values in the Problem Set. Results plotted in Figure 7. The movie is showed in `q3-3.mp4`.

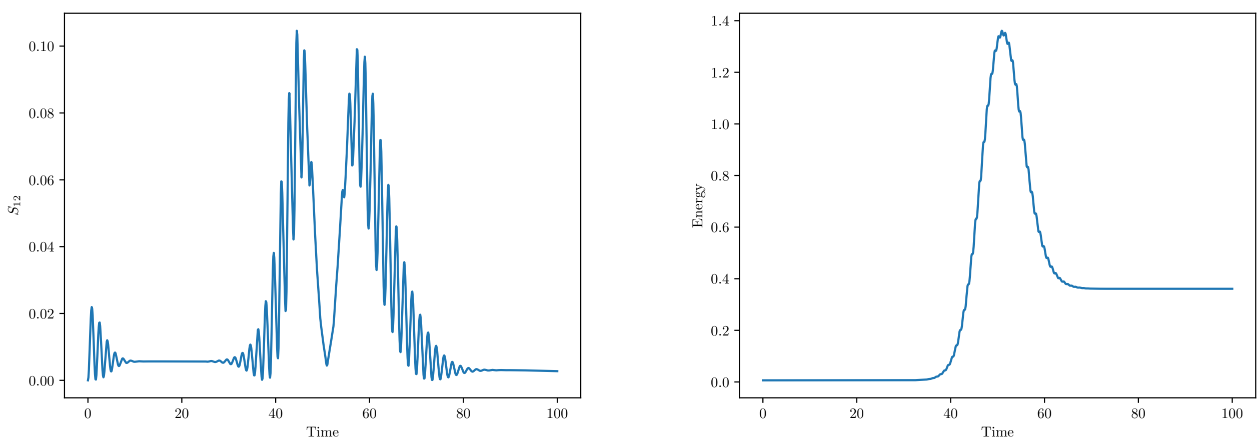


Figure 7

The wavepacket on $|1\rangle$ is vertically excited to $|2\rangle$ as the laser activate, and then gradually moves to the minimum points of the potential surface of $|2\rangle$ and hops back to $|1\rangle$.