Quantum Chemistry 1. exam February 24 2023

Chemicum A128, 9:00-12:00

1. One-dimensional quantum mechanical harmonic oscillator Hamiltonian of a diatomic molecule is $\hat{H} = \hat{T} + \hat{V} = \frac{1}{2\mu}\hat{p}_x^2 + \frac{1}{2}f_2 x^2$

   (a) Define the operator $\hat{p}_x$ and parameters μ and f_2 with their explicit expressions and describe in a few words their physical interpretations. What is the volume element for integration?

   (b) Compute the commutators $[\hat{H}, \hat{T}]$ and $[\hat{H}, \hat{V}]$.

   (c) Explain carefully what physically the results in (b) mean.

2. Two-dimensional quantum mechanical vibrational harmonic oscillator Hamiltonian is $\hat{H} = \hat{H}_x + \hat{H}_y = (\frac{1}{2\mu}\hat{p}_x^2 + \frac{1}{2}f_2 x^2) + (\frac{1}{2\mu}\hat{p}_y^2 + \frac{1}{2}f_2 y^2)$

   (a) Give an example of a molecular system that is described by this Hamiltonian model. What is the value of $[\hat{H}_x, \hat{H}_y]$? Interpret the result.

   (b) What are the energies and the wavefunctions of the Hamiltonian?

   (c) What is the degeneracy of this system, if the total vibrational quantum number is 5?

3. A quantum mechanical particle is in a box with the width l and infinitely high walls.

   (a) Derive the energy level expression $E_n = \frac{n^2 h^2}{8ml^2}$.

   (b) The particle is in a state described by the wavefunction $\Psi = \frac{1}{\sqrt{2}}\psi_1 + \frac{1}{\sqrt{2}}\psi_2$, where the eigenfunction ψ_i corresponds to E_i in (a). Is this state a stationary one? What is the expectation value of the energy? What is the value and probability if we make a single measurement of the energy?

   (c) Let $t > 0$ s. Give the wavefunction $\Psi(x,t)$ as a linear combination of the time-independent eigenfunctions ψ_i, when the wavefunction is given in (b) at $t = 0$ s. Does $\Psi(x,t)$ describe a stationary state? What is the expectation value of the energy? What is the outcome if we make a single measurement of the energy?

3. A study is seeking to model the performance of primary school pupils in a shared exam. The performance of pupils from school i is denoted by X_i, $i = 1, \ldots, k$.

   The performance X_i is assumed to depend on global exam-specific effect $\theta_0 \sim N(\mu, \sigma_0^2)$, as well as a school-specific effect $\theta_i \sim N(0, \sigma^2), i = 1, \ldots, k$. These are all assumed to the independent. Here $N(\mu, \sigma^2)$ denotes a univariate normal distribution with mean μ and variance σ^2.

   Assuming $X_i = \theta_0 + \theta_i$, evaluate the following quantities:

   i. $\mathbb{E}(X_i)$.

   ii. $\mathbb{V}(X_i)$.

   iii. $\text{Cov}(X_i, X_j), i \neq j$.

4. Let $\hat{\theta}_1$ and $\hat{\theta}_2$ be two independent estimators with corresponding standard errors $\text{se}(\hat{\theta}_1)$ and $\text{se}(\hat{\theta}_2)$.

   i. Evaluate the standard error $\text{se}(\hat{\theta}_1 - \hat{\theta}_2)$.

   ii. Explain how you could use this to construct an approximate $1 - \alpha$ confidence interval for $\theta_1 - \theta_2$.

   iii. Explain how you can use this to perform a Wald test at approximate level α for testing against the null $H_0 : \theta_1 = \theta_2$.

5. An e-commerce company is developing their site by running experiments. They run 5 different versions of their site on Monday, Tuesday, Wednesday, Thursday and Friday, a different one on each day. They observe the average amount of purchases of the visitors to decide which version is the best, and start using that in production (as well as as a basis for the next round of experiments). Despite a lot of effort, the company is unhappy with the results and has hired you as a consultant to improve their process.

   i. What weaknesses are there in the experimental approach the company is using?

   ii. How could you improve the data collection to increase the likelihood of identifying which of the 5 versions would likely yield the largest sales when applied in production and predicting if they are likely to improve the sales over the existing design?

   iii. Which methods would you propose using to analyse the data collected using the procedure you proposed in (ii).