

The Harmonic Oscillator with a Gaussian Perturbation: Evaluation of the Integrals and Example Applications

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The harmonic oscillator with a Gaussian perturbation is an interesting model problem in its own right, and it has been of practical interest in relation to the problem of frequency “doubling” in the vibrational spectrum of ammonia. This latter problem has been addressed by numerous authors over the years, with at least two (1, 2) using a potential function of the type described here. In this article, we derive a general result for the matrix elements of this perturbation and apply it to an ad hoc pedagogical example. Application to the ammonia problem is summarized, with full details available in the online supplement.

Problems in perturbation theory that are both interesting and tractable for use in courses are not numerous, as any teacher of quantum mechanics or quantum chemistry may attest. Often, the factor that determines pedagogical suitability is the effort involved in evaluating the required integrals. One system that has been widely studied is the perturbed harmonic oscillator (e.g., 3, 4). In one case, an analytical result for a particular type of perturbation integral has been found (4), in a similar spirit to the present article. Here, the harmonic oscillator with a Gaussian perturbation is considered. This perturbation provides a central barrier in the potential well that is easily adjustable in both width and height. As will be shown, the fact that the perturbation is Gaussian in form allows an analytical expression to be found for the integrals.

Although I have not seen this problem discussed in any textbook, it does appear in a monograph (1) and in the primary literature (2). However, in these two cases, the method of evaluating the matrix elements is sufficiently cumbersome to limit its pedagogical utility. In the first case, the Gaussian perturbation function is expanded as a power series, and each term is integrated individually using standard Gaussian integral formulas. This gives only an approximation of each matrix element. In the second case, the integral for each pair of states is evaluated directly using Gaussian integral formulas. This is tractable for a few states, but rapidly becomes cumbersome. Both of these authors applied the results to the problem of “inversion doubling” in the ammonia vibrational spectrum. This is due to an umbrella-like inversion motion of the molecule, such that the two individual potential wells for the normal coordinate(s) of interest (primarily the umbrella motion, v_2) are separated by a barrier whose height represents the energy barrier to inversion (5).

My interest in this problem originated when I used it a couple of times on exam questions in quantum chemistry. Based on my experience with generating functions, it seemed likely that a general result for the integrals might be found in this way. This proved to be so, and the results are described.

Evaluation of the Integrals

The Hamiltonian for a one-dimensional harmonic oscillator of mass m , with an added Gaussian perturbation term, may be written

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 + b \exp(-cx^2) \quad (1)$$

where k is the force constant of the unperturbed oscillator and b and c are parameters that control, respectively, the height and width of the perturbation function. For ease of notation, and as it is required for numerical computation, the operator may be expressed in terms of the dimensionless variable $y = \alpha^{1/2} x$, with $\alpha = m\nu_0/\hbar$, where ν_0 is the natural frequency of the oscillator in Hz,

$$\hat{H} = -\frac{b\nu_0}{2} \frac{d^2}{dy^2} + \frac{1}{2} b\nu_0 y^2 + b\nu_0 \beta \exp(-\gamma y^2) \quad (2)$$

where $b\nu_0\beta = b$, and $\alpha\gamma = c$.

The Schrödinger equation may then be written

$$\left[-\frac{1}{2} \frac{d^2}{dy^2} + \frac{1}{2} y^2 + \beta \exp(-\gamma y^2) \right] \Psi = \frac{E}{b\nu_0} \Psi \quad (3)$$

The operator on the left is the total energy operator in units of the quantum of energy $b\nu_0$.

The integrals required for finding an approximate solution to this problem using the harmonic oscillator (HO) basis functions are, neglecting the pre-exponential factor β ,

$$\begin{aligned} V_{nm} &= \int_{-\infty}^{\infty} \Psi_n(\alpha^{1/2} x) \Psi_m(\alpha^{1/2} x) \exp(-cx^2) dx \\ &= \frac{1}{\alpha^{1/2}} \int_{-\infty}^{\infty} \Psi_n(y) \Psi_m(y) \exp(-\gamma y^2) dy \end{aligned} \quad (4)$$

In terms of the Hermite polynomials, this becomes

$$V_{nm} = \frac{N_n N_m}{\alpha^{1/2}} \int_{-\infty}^{\infty} H_n(y) H_m(y) \exp[-(\gamma + 1)y^2] dy \quad (5)$$

where N_n is the normalization constant for the n th unperturbed HO wavefunction.

The generating function for the Hermite polynomials is defined by

$$\exp\left[y^2 - (z - y)^2\right] = \sum_{n=0}^{\infty} \frac{H_n(y)}{n!} z^n \quad (6)$$

This allows us to write the equation

$$\begin{aligned} & \frac{N_n N_m}{\alpha^{1/2}} \int_{-\infty}^{\infty} \exp\left[y^2 - (z - y)^2\right] \times \\ & \exp\left[y^2 - (t - y)^2\right] \exp\left[-(\gamma + 1)y^2\right] dy \\ & = \frac{N_n N_m}{\alpha^{1/2}} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \left\{ \int_{-\infty}^{\infty} \frac{H_n(y) H_m(y)}{n! m!} \times \right. \\ & \left. \exp\left[-(\gamma + 1)y^2\right] dy \right\} z^n t^m \end{aligned} \quad (7)$$

$$\begin{aligned} & \frac{N_n N_m}{\alpha^{1/2}} \int_{-\infty}^{\infty} \exp\left[y^2 - (z - y)^2\right] \times \\ & \exp\left[y^2 - (t - y)^2\right] \exp\left[-(\gamma + 1)y^2\right] dy \quad (8) \\ & = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} V_{nm} z^n t^m \end{aligned}$$

We focus now on the left-hand side (LHS) of this equation. Simplifying the exponent yields

$$\begin{aligned} \text{LHS} &= \frac{N_n N_m}{\alpha^{1/2}} \int_{-\infty}^{\infty} \exp\left[-(\gamma + 1)y^2 + (2z + 2t)y\right] dy \\ &= \frac{N_n N_m}{\alpha^{1/2}} \left(\frac{\pi}{1 + \gamma}\right)^{1/2} \exp\left[\frac{(z + t)^2}{(1 + \gamma)}\right] \exp(-z^2 - t^2) \end{aligned} \quad (9)$$

where the integration was performed using a standard formula (6).

The next task is to collect terms in the exponent in preparation for expressing the exponential as a product of power series. This yields

$$\begin{aligned} \text{LHS} &= \frac{N_n N_m}{\alpha^{1/2}} \left(\frac{\pi}{1 + \gamma}\right)^{1/2} \times \\ & \exp\left(\frac{-\gamma z^2}{1 + \gamma}\right) \exp\left(\frac{-\gamma t^2}{1 + \gamma}\right) \exp\left(\frac{2zt}{1 + \gamma}\right) \end{aligned} \quad (10)$$

Thus,

$$\begin{aligned} \text{LHS} &= \frac{N_n N_m}{\alpha^{1/2}} \left(\frac{\pi}{1 + \gamma}\right)^{1/2} \times \\ & \sum_{j=0}^{\infty} \frac{z^{2j}}{j!} \left(\frac{-\gamma}{1 + \gamma}\right)^j \sum_{k=0}^{\infty} \frac{t^{2k}}{k!} \left(\frac{-\gamma}{1 + \gamma}\right)^k \sum_{l=0}^{\infty} \frac{\left(\frac{2zt}{1 + \gamma}\right)^l}{l!} \end{aligned} \quad (11)$$

$$\begin{aligned} \text{LHS} &= \frac{N_n N_m}{\alpha^{1/2}} \left(\frac{\pi}{1 + \gamma}\right)^{1/2} \times \\ & \sum_{j,k,l} \frac{\gamma^{j+k}}{(1 + \gamma)^{j+k+l}} \frac{(-1)^{j+k} 2^l z^{2j+l} t^{2k+l}}{j! k! l!} \end{aligned} \quad (12)$$

From eq 8 both sides are now expressed as power series in z and t :

$$\begin{aligned} & \frac{N_n N_m}{\alpha^{1/2}} \left(\frac{\pi}{1 + \gamma}\right)^{1/2} \times \\ & \sum_{j,k,l} \frac{\gamma^{j+k}}{(1 + \gamma)^{j+k+l}} \frac{(-1)^{j+k} 2^l z^{2j+l} t^{2k+l}}{j! k! l!} = \sum_{n,m} V_{nm} z^n t^m \end{aligned} \quad (13)$$

Equating powers of z and t gives us the result for V_{nm} :

$$\begin{aligned} V_{nm} &= n! m! N_n N_m \left[\frac{\pi}{\alpha(1 + \gamma)}\right]^{1/2} \times \\ & \sum_{j,k,l} \frac{\gamma^{j+k}}{(1 + \gamma)^{j+k+l}} \frac{(-1)^{j+k} 2^l}{j! k! l!} \delta_{n,2j+l} \delta_{m,2k+l} \end{aligned} \quad (14)$$

Using the explicit expression for N_n ,

$$N_n = \left(\frac{\alpha}{\pi}\right)^{1/4} \left(\frac{1}{2^n n!}\right)^{1/2} \quad (15)$$

yields the final result

$$\begin{aligned} V_{nm} &= \left[\frac{n! m!}{2^{n+m} (1 + \gamma)}\right]^{1/2} \times \\ & \sum_{j,k,l} \frac{\gamma^{j+k}}{(1 + \gamma)^{j+k+l}} \frac{(-1)^{j+k} 2^l}{j! k! l!} \delta_{n,2j+l} \delta_{m,2k+l} \end{aligned} \quad (16)$$

A few comments may be helpful in applying this result. Since $V_{nm} = 0$ unless n and m are both even or both odd, each nonzero integral will involve only even or odd values of l . The minimum value of l is either 0 or 1, and the maximum value is the lesser of n or m . The number of possible values of l determines the number of terms in the summation. For example, in evaluating V_{57} , there are three terms: $l = 1, j = 2, k = 3$; $l = 3, j = 1, k = 2$; $l = 5, j = 0, k = 1$. All terms are of the same sign; in this case all terms are negative, since $(j + k)$ is odd in each term. The value of $j + k + l = (n + m)/2$, so all terms have a common factor of $(1 + \gamma)^{-(n+m+1)/2}$. The result for V_{57} is

$$V_{57} = -\left(\frac{1}{1 + \gamma}\right)^{13/2} \sqrt{42} \left(\frac{\gamma}{2} + \frac{5\gamma^3}{4} + \frac{5\gamma^5}{16}\right) \quad (17)$$

The formulas for all the integrals involving the first 10 states, which are used in the example discussed below, have been

Table 1. Results for Example Problem for the First Six Levels for Values of (β, γ) of 1, 3, and 5

State	N	(1,5)			(3,5)			(5,5)		
		V(3)	V(5)	P(2)	P(3)	N	V(3)	V(5)	P(2)	P(3)
0	0.8649	0.8691	0.8658	0.8675	0.8653	1.3445	1.3603	1.3472	1.3584	1.2987
1	1.5634	1.5647	1.5639	1.5637	1.5639	1.6670	1.6754	1.6699	1.6649	1.6701
2	2.6698	2.6754	2.6713			3.0738	3.1225	3.0834		
3	3.5701	3.5726	3.5710			3.6948	3.7138	3.7010		
4	4.6063	4.6146	4.6082			4.8776	4.9945	4.8952		
5	5.5671	5.5717	5.5685			5.6936	5.7376	5.7046		
State	N	(1,3)			(3,3)			(5,3)		
		V(3)	V(5)	P(2)	P(3)	N	V(3)	V(5)	P(2)	P(3)
0	0.95025	0.9528	0.9506	0.9542	0.9501	1.5365	1.5419	1.5368	1.5883	1.4767
1	1.6148	1.6163	1.6151	1.6146	1.6151	1.7936	1.8025	1.7953	1.7814	1.7952
2	2.6947	2.7002	2.6957			3.1964	3.2363	3.2010		
3	3.6105	3.6141	3.6114			3.8101	3.8341	3.8156		
4	4.6225	4.6329	4.6245			4.9388	5.0795	4.9536		
5	5.5965	5.6044	5.5984			5.7858	5.8652	5.7985		
State	N	(1,1)			(3,1)			(5,1)		
		V(3)	V(5)	P(2)	P(3)	N	V(3)	V(5)	P(2)	P(3)
0	1.1661	1.1663	1.1661	1.1725	1.1668	2.1339	2.1356	2.1341	2.3094	2.1575
1	1.8257	1.8261	1.8257	1.8256	1.8255	2.3219	2.3223	2.3219	2.3090	2.3058
2	2.7783	2.7822	2.7784			3.4958	3.5055	3.4958		
3	3.7239	3.7281	3.7241			4.1723	4.1914	4.1926		
4	4.6976	4.7172	4.6989			5.1431	5.3558	5.1471		
5	5.6767	5.6943	5.6782			6.0472	6.2319	6.0529		

NOTE: Energy values in units of the quantum of the unperturbed potential for various computational approaches. N: Precise numerical solutions using the Numerov procedure. V(3): Variational approximation using three states of each symmetry. V(5): Variational approximation using five states of each symmetry. P(2): Second-order perturbation theory result using five states of each symmetry. P(3): Third-order perturbation theory result using five states of each symmetry.

entered into Mathcad documents, which are available in the online supplement.

With the ability to easily calculate all the matrix elements, we can now attack the problem for a specific perturbation in any one of three ways: numerically, which will provide the eigenvalues to arbitrary precision; variationally, that is, diagonalize a sub-matrix of the entire Hamiltonian matrix of any desired size; or by using perturbation theory to any order, including any number of interacting states in the summations. Thus the problem provides an excellent pedagogical illustration of the comparison of these various approaches.

A Simple Example

This is an ad hoc example that I have used as a problem assignment to compare the various techniques for arriving at approximations to the energy eigenvalues for a particular Hamiltonian. The numerical solution used a Numerov procedure, as described in Levine (7). The implementation of the procedure was carried out in Mathcad (8) rather than using a spreadsheet. (All computations described here were done in Mathcad. The documents used are available in the online supplement.) Approximate results were obtained using 3×3 and 5×5 variational calculations as well as perturbation theory to 2nd and 3rd order, including the first ten states in the relevant summations. With the expressions for the integrals entered into a Mathcad document, it is quite trivial to explore the effects of changing the parameters of the perturbation, so there is plenty of room to investigate how the height and width of the barrier change the energy states, as well as how the performance of variational and perturbation approximations vary with the nature of the potential. The results for the first six levels for values of β and γ of 1, 3, and 5 are shown in Table 1.

This table is arranged from the mildest perturbation, $\exp(-5\gamma^2)$, at the upper left, to the strongest, $5\exp(-\gamma^2)$, at the lower right. Some interesting features are apparent. As expected, the perturbation affects the even states much more than the odd states; for moderate perturbations, the original spacing of one unit is retained almost exactly even for the lowest odd states. As a result, the two lowest states are closer together, which pattern, if continued for more profound perturbations, leads to the “doubling” phenomenon. For the two lowest levels, the separation under the effect of the strongest perturbation is reduced to about 4% of its unperturbed value.

The experience of setting up and carrying out the calculation in Mathcad convinces one that the variational method is superior in terms of convenience, given that a numerical routine for finding the roots of the secular determinant is available. (The roots were found using the eigvals function.) The 5×5 variational calculation agrees quite well with the numerical results for all the states shown, so the effect of including the additional states in the basis set is evident. One interesting aspect of the perturbation theory results is that for the lowest state the third-order contribution is negative, so the approximate result is in fact lower than the “true” ground state energy in several cases. Except for the strongest perturbations, the ground-state corrected to third order compares favorably with the higher-level variational result.

As the material presented here was developed recently, I have had only two opportunities to use it as an assignment as described above. In those cases, I used only one potential, with

Table 2. Energies for the First 8 States of the Ammonia v_2 Vibration

State	Experimental	This Exercise	“Best” ab initio (20)
GS ⁺	0	0	0
GS [−]	0.793	1.6	0.96
v^+	932.43	933	923
v^-	968.12	969	965
$2v^+$	1598.47	1659	1578
$2v^-$	1882.18	1890	1882
$3v^+$	2384.17	2401	2388
$3v^-$	2895.61	2844	2910

NOTE: Energies in wavenumbers.

$\beta = 2$, $\gamma = 5$. I provided the numerical solutions and asked the students to use eq 16 to generate the formulas for the integrals and then to obtain the variational and perturbation results. In both cases, the problem was part of the final problem set of the term. In the first case, a combination of logistical and other factors led to only two students in a class of eight completing the assignment with reasonable success. In the second case, both students in a class of two were able to achieve a fairly complete solution to this problem.

The Ammonia Problem

A “real-world” example is that of the inversion doubling in the umbrella motion of ammonia. This has been studied extensively over many decades (1, 2, 9–20), with recent high-level ab initio calculations of a potential surface that will reproduce the observed spectrum (19, 20). This section summarizes the results of a relatively simple approach in which the parameters of a Gaussian perturbation are fit to the spectroscopic data. While this will not do so well as more sophisticated methods in fitting the observed transitions, it is an approach that can be carried out relatively easily using a program such as Mathcad. The values that best fit the experimental data were found to be $\gamma = 0.2754$ and $\beta = 2.993$. By comparing the Numerov results to the experimental data, one quantum of the unperturbed potential was found to be equivalent to 605.9 cm^{-1} . Then one can translate the energies of all the levels found in the Numerov procedure into wavenumbers. This gives the results shown in Table 2 for the first eight levels. Mathematical details are provided in the online supplement.

The approximations to the first eight levels from variational and perturbation calculations compared to the Numerov results are shown in Table 3. This perturbation is “medium” in barrier height compared to those considered in the first example, but decays much more gradually, so it has a much more profound effect. As a result, perturbation theory is, not surprisingly, an rather abject failure. The 5-state variational calculation works quite well for the lowest three states of each symmetry. However, the 3-state variational calculation fails rather badly for all the even states, working fairly well for only the lowest odd state. Because of this contrast, I did a 4-state variational calculation, which works well for the two lowest states, but exhibits problems for the second even state, while doing quite well for the second odd state.

Table 3. Results for the Ammonia Example

State	Numerical ^a	Variational (3 x 3)	Variational (4 x 4)	Variational (5 x 5)	Perturbation ^b (2nd order)	Perturbation ^b (3rd order)
0 (GS ⁺)	5.36699	5.48138	5.36730	5.36727	7.09	6.39
1 (GS ⁻)	5.36964	5.38651	5.37047	5.36966	6.00	5.24
2 (v ⁺)	6.90660	7.55940	6.98083	6.90804		
3 (v ⁻)	6.96550	7.34299	6.97244	6.96721		
4 (2v ⁺)	8.10526	9.60969	8.43311	8.11426		
5 (2v ⁻)	8.48632	10.25517	8.76007	8.48756		
7 (3v ⁺)	9.32956		11.04981	9.55414		
8 (3v ⁻)	10.06072		11.83977	10.24293		

^aEnergies given in units of the quantum of the unperturbed potential for various computational approaches.

^bCalculated using 5 states of each symmetry

The value of the central barrier height found when the potential parameters are fit as described above is 2180 cm⁻¹. Published work on this problem has focused on this value as the most significant feature of the potential. Values from about 1800 cm⁻¹ to about 2200 cm⁻¹ have been reported. A recent high-level ab-initio calculation (20), from which results are quoted in Table 2, achieved the best reproduction of the experimental data with a barrier height of 1867 cm⁻¹. These authors quoted an “experimental” value for the barrier height of 1885 cm⁻¹ (18). Of course, there is no such thing as an experimental value of the barrier height. A barrier height may be found from a theoretical calculation or from fitting an assumed analytic form of the potential function to the experimental spectroscopic data. The 1885 cm⁻¹ value is of the second type and results from perhaps the most elaborate and exhaustive effort of this type to date. Most recent efforts have given results in the 1850–1900 cm⁻¹ range, considerably lower than a “state-of-the-art” calculation done in the early 1960s (2), which reported a value of 2020 cm⁻¹. That article, in which a Gaussian perturbation was used, fit the experimental energies to within 2 cm⁻¹ for the first eight levels. The value found in this exercise is clearly high by current standards, but compares relatively well with early work on this problem, which is nicely reviewed in ref 2.

Conclusions

This article presented a method not reported previously for evaluating the matrix elements for a harmonic oscillator with a Gaussian perturbation. This model problem is now much more accessible for pedagogical applications illustrating perturbation theory and the variational method. An example has been presented of the use of this method to compare the various approaches to finding energy eigenvalues. An additional example of the application to the ammonia inversion problem is presented in summary form.

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Supplement

Mathematical details of the Ammonia Example

Mathcad files for the Numerov procedure, the variation method solution, and the perturbation theory solution