

Energy of a perturbed rigid rotor

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We obtain the energies of the stationary states of a rigid rotor under weak and strong perturbations by means of Rayleigh–Schrödinger perturbation theory combined with the diagonal hypervirial and Hellmann–Feynman theorems that facilitate the calculation. We show analytic expressions for both expansions that are sufficiently general for most practical applications of the model.

1. Introduction

The rigid rotor in a classical external field has long been a suitable model for the estimation of moments of inertia [1–3], dipole moments [1–3], and polarizability anisotropies [3,4] of linear and symmetrical-top molecules from microwave spectra. Rayleigh–Schrödinger perturbation theory provides simple analytical expressions for the eigenvalues of a rotating molecule in terms of its structural parameters, quantum numbers, and the strength of the field [1–4]. This and other practical applications motivated that many authors derived perturbation corrections of increasingly larger order for weak-field expansions [4–15]. These series have nonzero radii of convergence that increase with the quantum numbers [10,16] and are therefore suitable for the investigation of physical phenomena involving excited states. For low-lying states and sufficiently strong fields the weak-field series may not converge or may converge too slowly for practical applications.

In addition, it is possible to construct an alternative series that is accurate for extremely strong fields [17–19]. Unlike the weak-field series the strong-field expansion appears to be asymptotically divergent; however, there are renormalized series that match the weak and strong regimes giving results as accurate as those obtained from nonperturbative approaches [9–11].

There are several algorithms that facilitate the calculation of analytical and numerical perturbation corrections of large order [5–15,17–20]. Among them we mention the method based on the diagonal hypervirial theorem and Hellmann–Feynman theorem that appears to be simpler and more powerful than the others

[8–11,20]. This hypervirial perturbative method (HPM) is a convenient choice when one is only interested in the energies of the stationary states and at most in some expectation values because it belongs to the class of perturbation theories that do not produce explicit wave functions [21,22].

There is a renewed interest in perturbed rigid rotors as they appear in statistical models for the calculations of capture rate coefficients for the interaction of ions with neutral molecules [23,24] and in brute force orientation of polar molecules in a molecular beam [25]. The perturbations in the former application are more complicated than the simple interaction between an electric field and a dipole.

The rotational and vibrational molecular motions are not separable, but the examples above show that under certain circumstances the perturbed rigid rotor model is acceptable, not just in the weak-field limit, but also for strong interactions.

In this paper we apply perturbation theory to a rigid rotor with a quite general perturbation that includes those mentioned above as particular examples. To this end we develop the HPM in a more convenient way generating both the weak- and strong-field expansions from only one eigenvalue equation (unlike previous approaches [8–11,20]). Moreover, we point out an intrinsic flexibility of perturbation theory with respect to the choice of the reference eigenvalue equation and to the grouping of terms in the interaction potential.

In section 2 we introduce the model and derive the eigenvalue equation that we use afterwards to generate the hypervirial recurrence relations for the weak- and strong-field expansions developed in sections 3 and 4, respectively. Finally, we set forth our conclusions in section 5.

2. The model

Throughout this paper we assume that the perturbed rigid rotor model provides a reasonable description of the physical phenomenon. For the sake of concreteness, we consider a symmetrical top with principal moments of inertia $I_A = I_B \neq I_C$. It is customary to describe its position in space by means of the three Euler's angles θ , ϕ , and χ [2], the first one giving the orientation of the body axis with respect to the z axis of a nonrotating system of coordinates. For most purposes it is sufficient to assume that the interaction is a periodic, even function of θ with a minimum at $\theta = 0$:

$$U(\theta + 2\pi) = U(\theta), \quad U(-\theta) = U(\theta), \quad U'(0) = 0, \quad U''(0) > 0. \quad (1)$$

Since it does not depend on ϕ and χ then the time-independent Schrödinger equation is separable and one exactly solves the eigenvalue equations for those angles leaving only the one for θ [2]:

$$\left\{ \frac{1}{\sin(\theta)} \frac{d}{d\theta} \sin(\theta) \frac{d}{d\theta} - \frac{[M - K \cos(\theta)]^2}{\sin(\theta)^2} - aK^2 - V(\theta) + \epsilon \right\} \Theta(\theta) = 0. \quad (2)$$

For simplicity we introduce the dimensionless quantities

$$a = I_A/I_C, \quad V(\theta) = 2I_A U(\theta)/\hbar^2, \quad \epsilon = 2I_A E/\hbar^2, \quad (3)$$

where E is the energy. The quantum numbers $M, K = 0, \pm 1, \pm 2, \dots$ in (2) have the usual meaning [2]. In the absence of interaction ($V = 0$) the dimensionless energy reads [2]

$$\epsilon(J, K) = (a - 1)K^2 + J(J + 1), \quad (4)$$

in which the remaining quantum number J is a positive integer greater than the greatest value between $|M|$ and $|K|$. The equations above apply to a spherical rotor if $a = 1$.

For the present purpose of the application of perturbation theory it is convenient to modify the eigenvalue equation (2) through the change of independent variable:

$$\Psi(\theta) = \sin(\theta)^{1/2} \Theta(\theta), \quad (5)$$

which leads to

$$\left[\frac{d^2}{d\theta^2} - \frac{\alpha}{\sin(\theta)^2} + \frac{\beta \cos(\theta)}{\sin(\theta)^2} - V(\theta) + \epsilon + (1 - a)K^2 + \frac{1}{4} \right] \Psi(\theta) = 0, \quad (6)$$

where

$$\alpha = M^2 + K^2 - \frac{1}{4}, \quad \beta = 2MK. \quad (7)$$

It is worth noticing that the new solution Ψ satisfies Dirichlet boundary conditions at $\theta = 0$ and $\theta = \pi$:

$$\Psi(0) = \Psi(\pi) = 0. \quad (8)$$

In subsequent sections we resort to (6) for the application of perturbation theory to a symmetrical top ($\beta \neq 0$) or to a linear rotor ($\beta = 0$).

3. Weak field

According to the properties of $U(\theta)$ we can expand $V(\theta)$ in a Fourier series of $\cos(j\theta)$. However, for the present application of perturbation theory it is convenient to consider the equivalent power series

$$V(\theta) = \sum_{j=0}^{\infty} V_j \cos(\theta)^j. \quad (9)$$

Perturbation theory gives us the freedom to rearrange the interaction potential in many different ways. In order to introduce a perturbation parameter to keep track of the perturbation corrections we simply substitute

$$\sum_{j=0}^{\infty} V_j \xi^j \cos(\theta)^j \quad (10)$$

for the expansion (9) and set the dummy perturbation parameter ξ equal to unity in the resulting expression for the energy. This strategy is consistent with the assumption that the potential coefficients V_j decrease with j . The Fourier series provides another example of grouping (the sum of terms $V'_j \xi^j \cos(j\theta)$) that we do not consider here because it leads to less simple HPM equations.

To facilitate the application of perturbation theory we make use of the hypervirial and Hellmann-Feynman theorems outlined in the appendix. The set of functions

$$f_j(\theta) = \sin(\theta) \cos(\theta)^j, \quad j = 0, 1, \dots, \quad (11)$$

is sufficient for that purpose because every $f_j(\theta)$ vanishes at $\theta = 0$ and $\theta = \pi$ and removes the denominator $\sin(\theta)^2$ in the second and third terms of (6) from the hypervirial relations. In this way we obtain a recurrence relation for the integrals

$$C^{(j)} = \int_0^\pi \Psi(\theta)^2 \cos(\theta)^j d\theta, \quad (12)$$

where we arbitrarily choose Ψ to be normalized to unity in $[0, \pi]$: $C^{(0)} = 1$. Substitution of (11) into (A.9) with $\eta\hbar^2 = 1$, $x = \theta$, and V given by (10) leads to

$$\begin{aligned} & (j+1) \left[2\mathcal{E} - \frac{1}{2}(j+1)^2 \right] C^{(j+1)} - \beta(2j+1)C^{(j)} \\ & + j(j^2 + 2\alpha - 2\mathcal{E} + 1)C^{(j-1)} - \frac{j}{2}(j-1)(j-2)C^{(j-3)} \\ & + \sum_{k=1}^{\infty} V_k \xi^k \left[(2j+k)C^{(j+k-1)} - (2j+k+2)C^{(j+k+1)} \right] = 0, \end{aligned} \quad (13)$$

where $j = 0, 1, \dots$, $C^{(i)} = 0$ if $i < 0$, and

$$\mathcal{E} = \epsilon + (1-a)K^2 - V_0 + \frac{1}{4}. \quad (14)$$

As indicated in the appendix we need the Hellmann-Feynman theorem

$$\frac{\partial \mathcal{E}}{\partial \xi} = \sum_{k=1}^{\infty} k \xi^{k-1} V_k C^{(k)} \quad (15)$$

in addition to the hypervirial theorem in order to complete the perturbation calculation.

Expanding the dimensionless energy and the expectation values in Taylor series about $\xi = 0$,

$$\mathcal{E} = \sum_{p=0}^{\infty} \mathcal{E}_p \xi^p, \quad C^{(j)} = \sum_{p=0}^{\infty} C_p^{(j)} \xi^p, \quad (16)$$

and collecting the coefficient of ξ^p in (13) and (15) we obtain a recurrence relation for the perturbation corrections:

$$\begin{aligned}
 C_p^{(j+1)} = & \frac{2}{(j+1)[4\mathcal{E}_0 - (j+1)^2]} \left\{ \beta(2j+1)C_p^{(j)} \right. \\
 & + j(2\mathcal{E}_0 - j^2 - 2\alpha - 1)C_p^{(j-1)} + \frac{j}{2}(j-1)(j-2)C_p^{(j-3)} \\
 & + 2 \sum_{s=1}^p \mathcal{E}_s \left[jC_{p-s}^{(j-1)} - (j+1)C_{p-s}^{(j+1)} \right] \\
 & \left. + \sum_{k=1}^p V_k \left[(2j+k+2)C_{p-k}^{(j+k+1)} - (2j+k)C_{p-k}^{(j+k-1)} \right] \right\} \quad (17)
 \end{aligned}$$

and a connection between the perturbation corrections to the energy and expectation values:

$$\mathcal{E}_{p+1} = \frac{1}{p+1} \sum_{k=1}^{p+1} k V_k C_{p-k+1}^{(k)}. \quad (18)$$

In order to calculate all the corrections to the energy through order r we use the recurrence relation (17) with $p = 0, 1, \dots, r-1$ and $j = 0, 1, \dots, r-p-1$ taking into account that $C_p^{(0)} = \delta_{p0}$ and that $C_s^{(i)} = 0$ if $s < 0$. At the end of every loop we calculate the corresponding correction to the energy by means of (18). The first three of them are

$$\mathcal{E}_1 = \frac{\beta}{2e} V_1, \quad (19)$$

$$\begin{aligned}
 \mathcal{E}_2 = & \frac{1}{8e^3(4e-3)} \left\{ (3\beta^2 + 5\beta^2e - 12de^2 + 4e^3) V_1^2 \right. \\
 & \left. + 4[3\beta^2 - 2(1+2d)e + 4e^2]e^2 V_2 \right\}, \quad (20)
 \end{aligned}$$

$$\begin{aligned}
 \mathcal{E}_3 = & \frac{\beta}{16e^5(4e-3)(e-2)} \left\{ [6\beta^2 + 19\beta^2e + (9\beta^2 - 24d)e^2 - 28de^3 + 20e^4] V_1^3 \right. \\
 & + 4[6\beta^2 + 7\beta^2e - 4(1+5d)e^2 + 12e^3]e^2 V_1 V_2 \\
 & \left. + 4[8 + 5\beta^2 + 4d - 6(3+2d)e + 12e^2]e^4 V_3 \right\}, \quad (21)
 \end{aligned}$$

which we decided to write in terms of

$$e = \mathcal{E}_0 - \frac{1}{4} = J(J+1), \quad d = \alpha + \frac{1}{4} = M^2 + K^2 \quad (22)$$

to simplify the resulting expressions. We have calculated perturbation corrections of larger order that we do not show here because they are too long. Aided by avail-

able software for computer algebra one obtains as many analytical corrections as the computer memory supports through eqs. (17) and (18). Finally, we write the rotational energy in terms of the quantum numbers, the molecular parameters, and the potential-energy coefficients as

$$E(J, M, K) = \frac{\hbar^2}{2I_A} \left(V_0 + J(J+1) + (a-1)K^2 + \sum_{j=1} \varepsilon_j \right). \quad (23)$$

For appropriate particular choices of the potential-energy coefficients the expressions above reduce to those used in the calculation of moments of inertia, dipole moments, polarizability anisotropies, and capture rate coefficients [1–4,23,24].

Former applications of the HPM have been based on generalized hypervirial relations for Sturm–Liouville eigenvalue equations [8–11,20]; here we have resorted to a much simpler Schrödinger equation in one dimension.

4. Strong field

When the potential well $V(\theta)$ is sufficiently deep the stationary states with energy much lower than the potential barrier become localized about the minimum at $\theta = 0$ and the probability of tunneling is negligible. Such states resemble those of an anharmonic oscillator more than the rigid rotor ones. If we met such conditions in classical mechanics we would try an approach based on small oscillation amplitudes. The same strategy applies in quantum mechanics as we show in what follows. The accuracy of this approximation increases not only with the depth of the well but also with the moments of inertia of the molecule suggesting that it is a semiclassical approach in agreement with the fact that tunneling is negligible.

In order to obtain the semiclassical series for the stationary states of the quasi-oscillator just described we expand the potential-energy function about its minimum at $\theta = 0$:

$$V(\theta) = \sum_{k=0}^{\infty} v_k \theta^{2k}. \quad (24)$$

For convenience we define

$$F(\theta) = \frac{\theta^2}{\sin(\theta)^2} = \sum_{j=0}^{\infty} F_j \theta^{2j}, \quad G(\theta) = F(\theta) \cos(\theta) = \sum_{j=0}^{\infty} G_j \theta^{2j}, \quad (25)$$

and obtain the expansion coefficients by means of the recurrence relations

$$F_n = \delta_{n0} - \sum_{j=1}^n \frac{(-1)^j 2^{2j+1}}{(2j+2)!} F_{n-j}, \quad G_n = \sum_{j=0}^n \frac{(-1)^j}{(2j)!} F_{n-j} \quad (26)$$

suitable for computer algebra.

After expanding every term of (6) in Taylor or Laurent series about $\theta = 0$ we define a new variable

$$q = \sqrt{\omega}\theta, \tag{27}$$

where ω plays the role of an oscillator frequency. Adding and subtracting q^2 to the expanded equation we finally have

$$\left(-\frac{d^2}{dq^2} + \frac{\alpha - \beta}{q^2} + q^2 - \tilde{\epsilon} + \sum_{j=1}^{\infty} u_j \zeta^j q^{2j} \right) \Psi = 0, \tag{28}$$

where

$$\tilde{\epsilon} = \frac{1}{\omega} \left[\epsilon + (1 - a)K^2 + \frac{1}{4} - \frac{2\alpha + \beta}{6} - v_0 \right], \tag{29}$$

$$u_j = \frac{1}{\omega} (v_j + \alpha F_{j+1} - \beta G_{j+1} - \omega^2 \delta_{j1}), \tag{30}$$

and ζ is a dummy perturbation parameter that we set equal to $1/\omega$ at the end of the calculation to recover the original eigenvalue equation. Since the change of variable (27) maps the interval $(0, \pi)$ onto $(0, \sqrt{\omega}\pi)$ and the application of perturbation theory about $\zeta = 0$ is equivalent to taking the limit $\omega \rightarrow \infty$ then the actual interval of the variable q is $(0, \infty)$. Solving the unperturbed equation

$$\left(-\frac{d^2}{dq^2} + \frac{\alpha - \beta}{q^2} + q^2 - \tilde{\epsilon}_0 \right) \Psi_0 = 0 \tag{31}$$

by means of any of the available textbook methods one obtains

$$\tilde{\epsilon}_0 = 4n + \sqrt{4(\alpha - \beta) + 1} + 2 = 2(2n + |M - K| + 1), \quad n = 0, 1, \dots \tag{32}$$

The diagonal hypervirial equation (A.9) with $\eta\hbar^2 = 1$, $x = q$, and $f = f_N = q^N$, $N = 0, 1, \dots$, gives us a recurrence relation for the expectation values

$$Q^{(N)} = \int_0^\infty \Psi(q)^2 q^{2N} dq \tag{33}$$

that we normalize according to $Q^{(0)} = 1$. Exactly as in the precedent case we expand $\tilde{\epsilon}$ and every $Q^{(N)}$ in Taylor series about $\zeta = 0$. The diagonal hypervirial relations lead to

$$Q_p^{(N+1)} = \frac{1}{4(N+1)} \left\{ N[4N^2 + 4(\beta - \alpha) - 1] Q_p^{(N-1)} + 2(2N+1) \sum_{s=0}^p \tilde{\epsilon}_s Q_{p-s}^{(N)} - 2 \sum_{j=1}^p (2N+j+1) u_j Q_{p-j}^{(N+j)} \right\}, \tag{34}$$

and from the Hellmann-Feynman theorem we obtain

$$\tilde{\mathcal{E}}_{p+1} = \frac{1}{p+1} \sum_{j=1}^{p+1} j u_j Q_{p-j+1}^{(j)}. \quad (35)$$

One easily calculates the corrections to the energy through order r from these two equations with $p = 0, 1, \dots, r-1$ and $N = 0, 1, \dots, r-p-1$. The first three ones are

$$\tilde{\mathcal{E}}_1 = \frac{\tilde{\mathcal{E}}_0}{2} u_1, \quad (36)$$

$$\tilde{\mathcal{E}}_2 = -\frac{\tilde{\mathcal{E}}_0}{8} u_1^2 + \frac{1}{2} \left(\frac{3}{4} + \alpha - \beta + \frac{3}{4} \tilde{\mathcal{E}}_0^2 \right) u_2, \quad (37)$$

$$\begin{aligned} \tilde{\mathcal{E}}_3 = & \frac{\tilde{\mathcal{E}}_0}{16} u_1^3 - \frac{1}{2} \left(\frac{3}{4} + \alpha - \beta + \frac{3}{4} \tilde{\mathcal{E}}_0^2 \right) u_1 u_2 \\ & + \frac{1}{4} \left[\frac{25}{4} + 3(\alpha - \beta) + \frac{5}{4} \tilde{\mathcal{E}}_0^2 \right] \tilde{\mathcal{E}}_0 u_3, \end{aligned} \quad (38)$$

where

$$u_1 = \frac{1}{\omega} \left(V_1 + \frac{8\alpha + 7\beta}{120} - \omega^2 \right), \quad (39)$$

$$u_2 = \frac{1}{\omega} \left(V_2 + \frac{32\alpha + 31\beta}{3024} \right), \quad (40)$$

$$u_3 = \frac{1}{\omega} \left(V_3 + \frac{128\alpha + 127\beta}{86400} \right). \quad (41)$$

One easily calculates many other perturbation corrections by means of eqs. (34) and (35) and straightforward computer algebra. The energy of the stationary states of the system read

$$E(n, M, K) = \frac{\hbar^2}{2I_A} \left[\omega \tilde{\mathcal{E}}_0 + (a-1)K^2 - \frac{1}{4} + \frac{2\alpha + \beta}{6} + V_0 + \tilde{\mathcal{E}}_1 + \sum_{p=1}^{\infty} \frac{\tilde{\mathcal{E}}_{p+1}}{\omega^p} \right]. \quad (42)$$

The choice of the parameter ω depends on the problem and on the particular application of the resulting expressions. This freedom illustrates the flexibility of perturbation theory with respect to the approximation of order zero. If interested in accurate numerical calculation one may set ω to improve the convergence of the series. In such a case the value of ω must depend on the number of terms in the expansion [22]. To obtain sufficiently accurate analytical expressions one simply chooses

$$\omega' = \sqrt{V_1 + (8\alpha + 7\beta)/120}, \quad (43)$$

which removes the correction of first order. On the other hand, the choice

$$\omega'' = \sqrt{V_1} = \frac{\sqrt{I_A U''(0)}}{\hbar} \quad (44)$$

most plainly reveals the semiclassical nature of the strong-field expansion as the perturbation parameter $1/\omega''$ is proportional to the Planck constant and is in inverse relation to the moment of inertia I_A . The accuracy of this expansion also increases with the curvature of the potential-energy function at its minimum.

5. Conclusions

We have considered the behaviour of a quantum-mechanical rigid rotor with a periodic perturbation under two extreme conditions. If the energy of the stationary state is much greater than the interaction then one applies the weak-field expansion. If, on the other hand, the energy of the stationary state is much lower than the potential barrier then the strongfield expansion is a better approximation. Therefore, when the interaction is smaller than the energy of the ground state of the free rotor the former approach applies to all states. However, if the interaction is sufficiently strong there will be states that clearly belong to one or the other description, and others with intermediate energies that are more difficult to treat because they may be beyond the range of validity of either expansion. In the latter case one may still obtain accurate results by means of properly renormalized series [9–11]. As stated before present results apply only when the perturbed rigid rotor is a suitable model for the physical phenomenon. Recent theoretical investigations assume that this is the case under certain circumstances [23– 25]. However, in other cases (or in more realistic approaches) one is forced to consider the effect of the perturbation on the molecular vibration. If one cannot assume total separability of the degrees of freedom then the HPM is not applicable.

The present discussion of the weak- and strong-field expansions for a perturbed rigid rotor is more general than previous treatments because we have not completely specified the interaction potential. Substituting particular potential coefficients for the undetermined ones V_j and v_i one obtains analytical expressions for the energies of most of the examples that appear in the literature [1– 4,20,23,24].

It has also been our purpose to reveal a great deal of freedom in perturbation theory with respect to the choice of the reference or unperturbed model as well as with regard to the rearrangement of the perturbation. The latter is in fact much more arbitrary and flexible than what we have shown here but an exhaustive discussion of this point is beyond the scope of this paper.

The HPM is a simple and powerful tool for the calculation of perturbation corrections to the energy of separable quantum- mechanical models. Unlike other approaches the HPM equations do not become more complicated as the terms of the potential energy function increase in number. Earlier numerical calculations

have shown that when the perturbation parameter is within the range of utility of the series, the perturbation expansion for perturbed rigid rotors is as accurate as the eigenvalues obtained by diagonalization of the Hamiltonian matrix [8–11]. Furthermore, it is possible to construct renormalized perturbation series that are valid for all values of the perturbation parameter [9–11]. The HPM is particularly suitable for the application of computer algebra allowing the calculation of many corrections in closed form. In the present paper we have derived the HPM equations for the weak- and strong-field expansions from just one simple eigenvalue equation instead of using one for each expansion as in former applications of the method [8–11,20]. In addition to this, the HPM recurrence relations derived here appear to be simpler than those used before.

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Appendix

To make this paper self-contained we briefly derive the main equations through which the hypervirial perturbative method (HPM) allows a simple and efficient calculation of the corrections of the Rayleigh–Schrödinger perturbation theory [21,22]. If Ψ is an eigenvector of the Hermitian operator H with eigenvalue E

$$H\Psi = E\Psi \quad (\text{A.1})$$

and A is a linear operator such that $A\Psi$ belongs to the domain of H then the diagonal hypervirial theorem reads [21]

$$\langle \Psi | [H, A] | \Psi \rangle = 0, \quad (\text{A.2})$$

in which $[H, A]$ denotes the commutator $HA - AH$. If the operator H depends on a parameter λ (which may be a charge, a mass, the intensity of an external field, etc.) then the Hellmann-Feynman theorem states that

$$\frac{\partial E}{\partial \lambda} \langle \Psi | \Psi \rangle = \langle \Psi | \frac{\partial H}{\partial \lambda} | \Psi \rangle. \quad (\text{A.3})$$

From now on we assume that $\langle \Psi | \Psi \rangle = 1$ and write $\langle A \rangle$ for $\langle \Psi | A | \Psi \rangle$.

The HPM applies only to one-dimensional or fully separable quantum-mechanical problems because only in such simple cases one can transform the diagonal hypervirial theorem into a recurrence relation for some set of functions of the coordinate operator. For concreteness we therefore assume that

$$H = \eta p^2 + V(x), \quad (\text{A.4})$$

where x and p are the coordinate and its conjugate momentum, respectively, ($[x, p] = i\hbar$) and η is a real positive number (such as, for example, $1/(2m)$, $1/(2I_A)$, etc.). Choosing

$$A = f(x)p + g(x), \quad (\text{A.5})$$

we easily prove that

$$[H, A] = \eta(2[p, f]p^2 + 2[p, g]p + [p, [p, f]]p + [p, [p, g]]) + f[V, p]. \quad (\text{A.6})$$

If

$$g = -\frac{1}{2}[p, f] \quad (\text{A.7})$$

then the terms that are linear in p in (A.6) cancel each other and we write

$$\langle [H, A] \rangle = -\frac{1}{2}\eta\langle [p[p, [p, f]]] \rangle + 2E\langle [p, f] \rangle - 2\langle [p, f]V \rangle - \langle f[p, V] \rangle = 0. \quad (\text{A.8})$$

In the coordinate representation $p = -i\hbar d/dx$ and (A.8) becomes

$$\frac{\eta\hbar^2}{2}\langle f''' \rangle + 2E\langle f' \rangle - 2\langle f'V \rangle - \langle fV' \rangle = 0. \quad (\text{A.9})$$

Sometimes it is necessary that $f(x)$ satisfies the boundary conditions for $A\Psi$ to belong to the domain of H . Suppose, for example, that the eigenfunctions of H are defined on the interval (x_1, x_2) , $-\infty < x_1 < x_2 < \infty$, and satisfy Dirichlet boundary conditions at the endpoints. Since $\Psi'(x)$ vanishes neither at x_1 nor at x_2 then $f(x)$ has to vanish at those points. This is in fact the case of the set of functions $f_j(\theta)$ used in section 3.

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