The Journal of Chemical Physics

A Practical Method for the Solution of Certain Problems in Quantum Mechanics by Successive Removal of Terms from the Hamiltonian by Contact Transformations of the Dynamical Variables Part II. Power Series in a Coordinate and Its Conjugate Momentum. The Anharmonic Oscillator by Perturbation Theory

L. H. Thomas

Citation: The Journal of Chemical Physics **10**, 538 (1942); doi: 10.1063/1.1723761
View online: http://dx.doi.org/10.1063/1.1723761
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/10/8?ver=pdfcov
Published by the AIP Publishing

A Practical Method for the Solution of Certain Problems in Quantum Mechanics by Successive Removal of Terms from the Hamiltonian by Contact Transformations of the Dynamical Variables

Part II. Power Series in a Coordinate and Its Conjugate Momentum. The Anharmonic Oscillator by Perturbation Theory

L. H. THOMAS
Mendenhall Laboratory of Physics, The Ohio State University, Columbus, Ohio
(Received December 18, 1941)

The non-commutative algebra of polynomials in a coordinate and its conjugate momentum is reduced to common algebra by Weyl's method, and tables are given for facilitating its use. It is shown how the problem of the anharmonic oscillator can be solved by contact transformations, and tables are given for removing terms up to the third degree in its coordinate and momentum and for finding the modified Hamiltonian up to the fourth degree, which is as far as is ordinarily required in molecular theory. To illustrate the power of the method, the energy is computed up to terms of the eighth degree for energy containing terms to that degree (in the coordinate only), obtaining Dunham's result together with the constant terms of that order not given by him.

4. POWER SERIES IN A COORDINATE AND ITS CONJUGATE MOMENTUM

IF

$$qp-pq=i\hbar \tag{4.1}$$

and if we deal only with terms up to the fourth degree in these variables, we may apply non-commutative algebra directly to expressions such as pqp^2 and take explicit account of relations such as $p^3q=pqp^2-2i\hbar p^2$. It is, however, convenient even here, and almost essential for extension to terms of higher degree, to adopt a definite convention for a standard combination of such terms as p^3q, p^2qp, pqp^2, and qp^3, and to construct a general theorem for combining these combinations.

We define $\{p^rq^s\}$ by the expansion

$$e^{\alpha p+\beta q}\equiv\sum_r\sum_s \alpha^r\beta^s\frac{\{p^rq^s\}}{r!s!}, \tag{4.2}$$

where α and β are ordinary numbers, so that, for instance,

$$\{p^2q^2\}\equiv \tfrac{1}{6}(p^2q^2+pqpq+pq^2p+qpqp+q^2p^2+qp^2q)$$

and $\{p^rq^s\}$ is $r!s!/(r+s)!$ times the sum of the $(r+s)!/r!s!$ terms distinct in non-commutative algebra which become p^rq^s in ordinary algebra.[1]

We shall write

$$\{\sum_{r,s} a_{rs}p^rq^s\}\equiv\sum_{r,s} a_{rs}\{p^rq^s\}$$

for a linear combination of terms of non-commutative algebra constructed in this way. With the aid of 4.1 any polynomial of non-commutative algebra can be expressed in this form in one and only one way (Table I). E.g.,

$$p^3q=\{p^3q-\tfrac{3}{2}i\hbar p^2\}$$
$$=\tfrac{1}{6}(p^3q+p^2qp+pqp^2+qp^3)-\tfrac{3}{2}i\hbar p^2.$$

TABLE I. $\hbar=1$, $[q,p]=1$.

$1=\{1\}$	$q^4=\{q^4\}$
$q=\{q\}$	$q^3p=\{q^3p+\tfrac{3}{2}iq^2\}$
$p=\{p\}$	$q^2pq=\{q^3p+\tfrac{1}{2}iq^2\}$
$q^2=\{q^2\}$	$qpq^2=\{q^3p-\tfrac{1}{2}iq^2\}$
$qp=\{qp+\tfrac{1}{2}i\}$	$pq^3=\{q^3p-\tfrac{3}{2}iq^2\}$
$pq=\{qp-\tfrac{1}{2}i\}$	$q^2p^2=\{q^2p^2+2iqp-\tfrac{1}{2}\}$
$p^2=\{p^2\}$	$qpqp=\{q^2p^2+iqp\}$
$q^3=\{q^3\}$	$qp^2q=\{q^2p^2+\tfrac{1}{2}\}$
$q^2p=\{q^2p+iq\}$	$pq^2p=\{q^2p^2+\tfrac{1}{2}\}$
$qpq=\{q^2p\}$	$pqpq=\{q^2p^2-iqp\}$
$pq^2=\{q^2p-iq\}$	$p^2q^2=\{q^2p^2-2iqp-\tfrac{1}{2}\}$
$qp^2=\{qp^2+ip\}$	$qp^3=\{qp^3+\tfrac{3}{2}ip^2\}$
$pqp=\{qp^2\}$	$pqp^2=\{qp^3+\tfrac{1}{2}ip^2\}$
$p^2q=\{qp^2-ip\}$	$p^2qp=\{qp^3-\tfrac{1}{2}ip^2\}$
$p^3=\{p^3\}$	$p^3q=\{qp^3-\tfrac{3}{2}ip^2\}$
	$p^4=\{p^4\}$

Reintroduce $\hbar$ in terms of degree $1/qp$ of the leading term, $\hbar^2$ in terms of degree $1/q^2p^2$, and so on.

[1] This definition follows H. Weyl, Zeits. f. Physik **46**, 1 (1927). The definition given by M. Born and P. Jordan, Zeits. f. Physik **34**, 858 (1925) and expanded by Born, Jordan, and Heisenberg, Zeits. f. Physik **35**, 557 (1926), leads to considerably more complicated results. It should be noted that we use differentiation only of the polynomials of common algebra.

TABLE II. $\hbar=1$, $[q,p]=1$, $[\{A\},\{B\}]=\{C\}$.

$A \backslash B$	q	p	q^2	qp	p^2	q^3	q^2p	qp^2	p^3
q	0	1	0	q	$2p$	0	q^2	$2qp$	$3p^2$
p	-1	0	$-2q$	$-p$	0	$-3q^2$	$-2qp$	$-p^2$	0
q^2	0	$2q$	0	$2q^2$	$4qp$	0	$2q^3$	$4q^2p$	$6qp^2$
qp	$-q$	p	$-2q^2$	0	$2p^2$	$-3q^3$	$-q^2p$	qp^2	$3p^3$
p^2	$-2p$	0	$-4qp$	$-2p^2$	0	$-6q^2p$	$-4qp^2$	$-2p^3$	0
q^3	0	$3q^2$	0	$3q^3$	$6q^2p$	0	$3q^4$	$6q^3p$	$9q^2p^2-3/2$
q^2p	$-q^2$	$2qp$	$-2q^3$	q^2p	$4qp^2$	$-3q^4$	0	$3q^2p^2+1/2$	$6qp^3$
qp^2	$-2qp$	p^2	$-4q^3p$	$-qp^2$	$2p^3$	$-6q^3p$	$-3q^2p^2-1/2$	0	$3p^4$
p^3	$-3p^2$	0	$-6qp^2$	$-3p^3$	0	$-9q^2p^2+3/2$	$-6qp^3$	$-3p^4$	0

Reintroduce $\hbar^2$ in terms of degree $1/q^2p^2$ of the leading term, $\hbar^4$ in terms of degree $1/q^4p^4$, and so on.

We make use of the lemma[2]

$$e^{\alpha p+\beta q}\equiv e^{\alpha p}e^{\beta q}e^{\frac{1}{2}i\hbar\alpha\beta}\equiv e^{\beta q}e^{\alpha p}e^{-\frac{1}{2}i\hbar\alpha\beta}, \tag{4.31}$$

or rather its corollary

$$e^{\alpha p+\beta q}e^{\gamma p+\delta q}=e^{(\alpha+\gamma)p}e^{(\beta+\delta)q}e^{\frac{1}{2}i\hbar(\beta\gamma-\alpha\delta)}, \tag{4.32}$$

to obtain the result, fundamental for working with polynomials in p and q, ($D_q(A)$ means $\partial/\partial q$ acting on A but not on B, and so on),

$$\begin{aligned}\{A\}\{B\}&\equiv\{e^{\frac{1}{2}i\hbar(D_q(A)D_p(B)-D_p(A)D_q(B))}AB\}\\ &\equiv\{AB\}+\tfrac{1}{2}i\hbar\left\{\frac{\partial A}{\partial q}\frac{\partial B}{\partial p}-\frac{\partial A}{\partial p}\frac{\partial B}{\partial q}\right\}\\ &\quad+\tfrac{1}{2}(\tfrac{1}{2}i\hbar)^2\left\{\frac{\partial^2 A}{\partial q^2}\frac{\partial^2 B}{\partial p^2}-2\frac{\partial^2 A}{\partial p\partial q}\frac{\partial^2 B}{\partial p\partial q}+\frac{\partial^2 A}{\partial p^2}\frac{\partial^2 B}{\partial q^2}\right\}\\ &\quad+\tfrac{1}{6}(\tfrac{1}{2}i\hbar)^3\left\{\frac{\partial^3 A}{\partial q^3}\frac{\partial^3 B}{\partial p^3}-3\frac{\partial^3 A}{\partial q^2\partial p}\frac{\partial^3 B}{\partial q\partial p^2}+3\frac{\partial^3 A}{\partial q\partial p^2}\frac{\partial^3 B}{\partial q^2\partial p}-\frac{\partial^3 A}{\partial p^3}\frac{\partial^3 B}{\partial q^3}\right\}+\cdots.\end{aligned} \tag{4.4}$$

In particular the Poisson bracket

$$\begin{aligned}[\{A\},\{B\}]&=\left\{\frac{\partial A}{\partial q}\frac{\partial B}{\partial p}-\frac{\partial A}{\partial p}\frac{\partial B}{\partial q}\right\}\\ &\quad+\tfrac{1}{6}(\tfrac{1}{2}i\hbar)^2\left\{\frac{\partial^3 A}{\partial q^3}\frac{\partial^3 B}{\partial p^3}-3\frac{\partial^3 A}{\partial q^2\partial p}\frac{\partial^3 B}{\partial q\partial p^2}+3\frac{\partial^3 A}{\partial q\partial p^2}\frac{\partial^3 B}{\partial q^2\partial p}-\frac{\partial^3 A}{\partial p^3}\frac{\partial^3 B}{\partial q^3}\right\}+\cdots.\end{aligned} \tag{4.5}$$

[2] H. Weyl, reference 1; the lemma follows from the properties of the group.

This last result connects quantum theory contact transformations with those of classical theory, enabling correction terms to be written down (Table II).

5. THE HARMONIC OSCILLATOR—EXCURSUS ON NOTATION

If

$$H=\frac{1}{2m}p^2+\frac{m\omega^2}{2}q^2, \tag{5.1}$$

where

$$qp-pq=i\hbar \tag{4.1}$$

the usual reduction of H to a diagonal matrix gives[3]

$$(n|H/k\omega|n)=n+\tfrac{1}{2}\quad n=0,1,2,\cdots \tag{5.21}$$

the remaining components vanishing,

$$\left(n+1\left|\frac{1}{\sqrt{\hbar}}(p/\sqrt{(m\omega)}+i\sqrt{(m\omega)}q)\right|n\right)=\sqrt{(2(n+1))}\quad n=0,1,2,\cdots \tag{5.22}$$

the remaining components vanishing,

$$\left(n\left|\frac{1}{\sqrt{\hbar}}(p/\sqrt{(m\omega)}-i\sqrt{(m\omega)}q)\right|n+1\right)=\sqrt{(2(n+1))}\quad n=0,1,2,\cdots \tag{5.23}$$

the remaining components vanishing.

[3] W. Heisenberg, Zeits. f. Physik **33**, 879 (1925); M. Born and P. Jordan, Zeits. f. Physik **34**, 858 (1925).

The derivation is:—if $H=\frac{1}{2}p^2+\frac{1}{2}q^2$, $qp-pq=i$; write $p+iq=\alpha$, $p-iq=\beta$, and $4H=\alpha\beta+\beta\alpha$, $\alpha\beta-\beta\alpha=2$; $H\alpha-\alpha H$ reduces to α; hence either $(n|\alpha|m)=0$ or $H_n-H_m=1$; and $(n|\alpha|m)(m|\beta|n)=|(n|\alpha|m)|^2=2H_n-1=2H_m+1$. The series $\cdots, H_m, H_m-1, H_m-2, \cdots$ must terminate since it must be positive, and can do so only for the value $\frac{1}{2}$; the values of H are $\cdots, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$; the representation can be chosen so that $(n+1|\alpha|n)$ and $(n|\beta|n+1)$ are real and positive, and the result follows.

These variables and matrices have been used for the examples of Part I of this paper.

Here we have used m for the mass of a particle moving under a restoring force proportional to the displacement such as to give a classical frequency of oscillation $\nu=\omega/2\pi$. This is customary in theoretical work. The use of $\hbar$ and ω removes most 2π's from the formulae.[4]

In applications to diatomic molecules it is usual to use μ for the reduced mass in place of m and to write $-kq$ for the restoring force so that we write

$$H=\frac{1}{2\mu}p^2+\frac{1}{2}kq^2. \tag{5.11}$$

It is usual to reserve ν for the actual wave number of a line (in cm^{-1}) rather than for the frequency (in rev./sec.), and to reserve ω for a value (in cm^{-1}) corresponding to the classical frequency for small oscillations.[5] If they occur in the same context we shall write ν_{osc} and ω_{osc} for the former, frequency of oscillation in rev./sec. and radians/sec., and $\tilde{\nu}$ and $\tilde{\omega}$ for the latter, observed wave number and corrected wave number, respectively.

For polyatomic molecules it is convenient to use dimensionless coordinates, $s=\sqrt{(m\omega_{\mathrm{osc}}/\hbar)}q$ with the corresponding momenta

$$p_s=\sqrt{(\hbar/m\omega_{\mathrm{osc}})}p$$

so that

$$H=\frac{1}{2}\hbar\omega_{\mathrm{osc}}(p_s{}^2/\hbar^2+s^2)=\frac{1}{2}\frac{\tilde{\omega}h}{c}(p_s{}^2/\hbar^2+s^2) \tag{5.12}$$

for the harmonic approximation for a single normal coordinate.[6]

For the purposes of this paper it is convenient to choose the unit of mass so that $m=1$, that of time so that $\omega=1$, and that of length so that $\hbar=1$, (this has already been done in Tables I and II). Thus we work with

$$H=\tfrac{1}{2}p^2+\tfrac{1}{2}q^2, \tag{5.13}$$

$$qp-pq=i. \tag{5.14}$$

To return to the usual units, replace p by $p/\sqrt{(m\hbar\omega)}$, q by $q\sqrt{(m\omega/\hbar)}$, H by $H/\hbar\omega$.

We can obtain the matrix components of $\{p^uq^v\}$ in the representation given by 5.21, 5.22, 5.23, as follows: From 5.22, 5.23,

$$(n+r|(p+iq)^r(p-iq)^s|n+s)=\frac{\sqrt{((n+r)!(n+s)!)}}{n!}2^{r+s/2}$$

$$n,\ r,\ s,\ \text{positive integers or zero,} \tag{5.3}$$

the remaining components vanishing. From

$$e^{\alpha(p+iq)+\beta(p-iq)}=e^{\alpha\beta}e^{\alpha(p+iq)}e^{\beta(p-iq)} \tag{4.31}$$

we obtain

$$\begin{aligned}(n+r|\{(p+iq)^r(p-iq)^s\}|n+s)&\\ &=\frac{\sqrt{((n+r)!(n+s)!)}}{n!}2^{r+s/2}\left(1+\frac{r\cdot s}{1\cdot(n+1)}\left(\frac{1}{2}\right)+\frac{r(r-1)s(s-1)}{1\cdot 2\cdot(n+1)(n+2)}\left(\frac{1}{2}\right)^2+\cdots\right)\\ &=\frac{\sqrt{((n+r)!(n+s)!)}}{n!}2^{r+s/2}F(-r,\ -s;n+1;\tfrac{1}{2})\end{aligned} \tag{5.4}$$

$n+r$, $n+s\geqslant 0$, the remaining components vanishing (if n is negative, the first $-n$ terms of the series

[4] P. A. M. Dirac, *Quantum Mechanics*, second edition (Oxford, 1934), pp. 90, 133; H. Weyl, *The Theory of Groups and Quantum Mechanics* (Methuen, 1931), p. 51.
[5] G. Herzberg, *Molecular Spectra and Molecular Structure* I (Prentice Hall, 1939), Chapter 3.
[6] S. Silver and W. H. Shaffer, J. Chem. Phys. 9, 599 (1941).

vanish); which, since

$$\{p^u q^v\} \equiv \sum_{s=0}^{u+v} \left\{\frac{(p+iq)^{u+v-s}(p-iq)^s}{2^{u+v}}\right\} \sum_b \frac{u!v!(-1)^b}{b!(r-s+b)!(s-b)!(v-b)!}$$

$$\equiv \sum_{s=0}^{u+v} \left\{\frac{(p+iq)^{u+v-s}(p-iq)^s}{2^{u+v}}\right\} \frac{u!}{s!(r-s)!} F(-s,\ -v;\ r-s+1;\ -1) \tag{5.5}$$

enables us to write down the matrix components of $\{p^u q^v\}$, e.g., returning to the usual units,

$$(n+4|\{p^3q^2\}|n+1) = \surd(m\omega)\left(\frac{\hbar}{2}\right)^{5/2} \tfrac{1}{2}(n+3)\surd((n+4)(n+3)(n+2)), \quad (n+2)\geqslant 0.$$

6. THE ANHARMONIC OSCILLATOR

If

$$H = \tfrac{1}{2}p^2 + \tfrac{1}{2}q^2 + \epsilon H_1(p, q), \tag{6.1}$$

where

$$qp - pq = i \tag{5.14}$$

we may remove a term $c\{p^r q^s\}$ from H_1 by a contact transformation to p^*, q^*, with a function $\epsilon c\{S\}$ given by

$$[\tfrac{1}{2}p^{*2} + \tfrac{1}{2}q^{*2},\ \{S\}] = \{p^{*r} q^{*s}\} \tag{6.21}$$

i.e., (4.5)

$$q^* \frac{\partial S}{\partial p^*} - p^* \frac{\partial S}{\partial q^*} = p^{*r} q^{*s} \tag{6.22}$$

so that the equation to find S is for the anharmonic oscillator of exactly the same form as in classical dynamics. (In returning to the usual units, replace S by $S/\hbar$). We then have (3.53)

$$H^* = H = \tfrac{1}{2}p^{*2} + \tfrac{1}{2}q^{*2} + \epsilon(H_1(p^*, q^*) + [c\{S\},\ \tfrac{1}{2}p^{*2} + \tfrac{1}{2}q^{*2}]) + \epsilon^2[c\{S\}, H_1(p^*, q^*)$$

$$+ \tfrac{1}{2}[c\{S\},\ \tfrac{1}{2}p^{*2} + \tfrac{1}{2}q^{*2}]] + \frac{\epsilon^3}{2}[c\{S\}, [c\{S\}, H_1(p^*, q^*) + \tfrac{1}{3}[c\{S\},\ \tfrac{1}{2}p^{*2} + \tfrac{1}{2}q^{*2}]]] + \cdots. \tag{6.3}$$

To save writing it is convenient to drop the asterisks, remembering that both $\{S\}$ and the transformed H are in terms of the transformed variables.

Thus for s odd we may take

$$S = \frac{p^{r+1}q^{s-1}}{(r+1)} + \frac{(s-1)}{(r+1)(r+3)} p^{r+3} q^{s-3} + \cdots + \frac{(s-1)\cdots 2}{(r+1)(r+3)\cdots(r+s)} p^{r+s} \tag{6.41}$$

and for r odd

$$S = -\frac{p^{r-1}q^{s+1}}{(s+1)} - \frac{(r-1)}{(s+1)(s+3)} p^{r-3} q^{s+3} - \cdots - \frac{(r-1)\cdots 2}{(s+1)(s+3)\cdots(s+r)} q^{s+r}. \tag{6.42}$$

If r and s are both odd, these two expressions differ by a multiple of $(p^2+q^2)^{r+s/2}$, and the sum of either and any multiple of this may be taken. (The transformation function reducing H to a function of $\tfrac{1}{2}p^{*2} + \tfrac{1}{2}q^{*2}$ is itself in fact only determined up to an additive function of $\tfrac{1}{2}p^{*2} + \tfrac{1}{2}q^{*2}$, though the reduced form of H is completely determined.)

If r and s are both even, $c\{p^r q^s\}$ cannot be removed, but can be reduced to $C\{(p^2+q^2)^{r+s/2}\}$. If $\sim$ means can be reduced to,

TABLE III.

$$
\begin{aligned}
\{q^2\} &\sim \tfrac{1}{2}\{(p^2+q^2)\} &&= \tfrac{1}{2}(p^2+q^2)\\
\{p^2\} &\sim \tfrac{1}{2}\{(p^2+q^2)\} &&= \tfrac{1}{2}(p^2+q^2)\\[4pt]
\{q^4\} &\sim \tfrac{3}{8}\{(p^2+q^2)^2\} &&= \tfrac{3}{8}((p^2+q^2)^2+1)\\
\{q^2p^2\} &\sim \tfrac{1}{8}\{(p^2+q^2)^2\} &&= \tfrac{1}{8}((p^2+q^2)^2+1)\\
\{p^4\} &\sim \tfrac{3}{8}\{(p^2+q^2)^2\} &&= \tfrac{3}{8}((p^2+q^2)^2+1)\\[4pt]
\{q^6\} &\sim \tfrac{5}{16}\{(p^2+q^2)^3\} &&= \tfrac{5}{16}((p^2+q^2)^3+5(p^2+q^2))\\
\{q^4p^2\} &\sim \tfrac{1}{16}\{(p^2+q^2)^3\} &&= \tfrac{1}{16}((p^2+q^2)^3+5(p^2+q^2))\\
\{q^2p^4\} &\sim \tfrac{1}{16}\{(p^2+q^2)^3\} &&= \tfrac{1}{16}((p^2+q^2)^3+5(p^2+q^2))\\
\{p^6\} &\sim \tfrac{5}{16}\{(p^2+q^2)^3\} &&= \tfrac{5}{16}((p^2+q^2)^3+5(p^2+q^2))\\[4pt]
\{q^8\} &\sim \tfrac{35}{128}\{(p^2+q^2)^4\} &&= \tfrac{35}{128}((p^2+q^2)^4+14(p^2+q^2)^3+9)\\
\{q^6p^2\} &\sim \tfrac{5}{128}\{(p^2+q^2)^4\} &&= \tfrac{5}{128}((p^2+q^2)^4+14(p^2+q^2)^2+9)\\
\{q^4p^4\} &\sim \tfrac{3}{128}\{(p^2+q^2)^4\} &&= \tfrac{3}{128}((p^2+q^2)^4+14(p^2+q^2)^2+9)\\
\{q^2p^6\} &\sim \tfrac{5}{128}\{(p^2+q^2)^4\} &&= \tfrac{5}{128}((p^2+q^2)^6+14(p^2+q^2)^2+9)\\
\{p^8\} &\sim \tfrac{35}{128}\{(p^2+q^2)^4\} &&= \tfrac{35}{128}((p^2+q^2)^4+14(p^2+q^2)^2+9)
\end{aligned}
$$

Replace p by $p/\sqrt{(m\hbar\omega)}$, q by $q\sqrt{(m\omega/\hbar)}$.

TABLE IV. $\hbar=1$, $[q, p]=1$, $[\tfrac{1}{2}(p^2+q^2), \{S\}]=\{H_1\}$

H_1	S	H_1	S
$1-1$	0	$q^4-\tfrac{3}{8}(p^2+q^2)^2$	$\tfrac{5}{8}q^3p+\tfrac{3}{8}qp^3$
		q^3p	$-\tfrac{5}{32}q^4+\tfrac{3}{16}q^2p^2+\tfrac{3}{32}p^4$
q	p	$q^2p^2-\tfrac{1}{8}(p^2+q^2)^2$	$-\tfrac{1}{8}q^3p+\tfrac{1}{8}qp^3$
p	$-q$	qp^3	$-\tfrac{3}{32}q^4-\tfrac{3}{16}q^2p^2+\tfrac{5}{32}p^4$
		$p^4-\tfrac{3}{8}(p^2+q^2)^2$	$-\tfrac{3}{8}q^3p-\tfrac{5}{8}qp^3$
$q^2-\tfrac{1}{2}(p^2+q^2)$	$\tfrac{1}{2}qp$		
qp	$-\tfrac{1}{4}q^2+\tfrac{1}{4}p^2$	q^5	$q^4p+\tfrac{4}{3}q^2p^3+\tfrac{8}{15}p^5$
$p^2-\tfrac{1}{2}(p^2+q^2)$	$-\tfrac{1}{2}qp$	q^4p	$-\tfrac{1}{5}q^5$
		q^3p^2	$\tfrac{1}{3}q^2p^3+\tfrac{2}{15}p^5$
q^3	$q^2p+\tfrac{2}{3}p^3$	q^2p^3	$-\tfrac{2}{15}q^5-\tfrac{1}{3}q^3p^2$
q^2p	$-\tfrac{1}{3}q^3$	qp^4	$\tfrac{1}{5}p^5$
qp^2	$\tfrac{1}{3}p^3$	p^5	$-\tfrac{8}{15}q^5-\tfrac{4}{3}q^3p^2-qp^4$
p^3	$-\tfrac{2}{3}q^3-qp^2$		

Replace p by $p/\sqrt{(m\hbar\omega)}$, q by $q\sqrt{(m\omega/\hbar)}$, H by $H/\hbar\omega$, S by $S/\hbar$.

$$
\{q^{2n}\}\sim\frac{2n-1}{1}\{q^{2n-2}p^2\}\sim\frac{(2n-1)(2n-3)}{1\cdot 3}\{q^{2n-4}p^4\}\sim\cdots\sim\{p^{2n}\}\sim\Big[\{(q^2+p^2)^n\}\Big/ 1+\frac{n}{1}\frac{1}{(2n-1)}+\frac{n(n-1)}{1\cdot 2}\frac{1\cdot 3}{(2n-1)(2n-3)}+\cdots+1\Big]=\{(q^2+p^2)^n\}\frac{1\cdot 3\cdots(2n-1)}{2\cdot 4\cdots 2n}. \tag{6.5}
$$

(Tables III and IV).

For the anharmonic oscillator the difference from classical mechanics enters in the Poisson brackets, (e.g., in the usual units, $[\{q^4p\}, \{qp^4\}]=\{15q^4p^4-6\hbar q^2p^2-\tfrac{3}{2}\hbar^2\}$ of which the first term only would occur in classical mechanics).

When H_1 can be expressed as a power series in p and q, a series for S is obtained reducing H to a power series in $\{(p^2+q^2)^n\}$ together with terms of higher order than ϵ; a second transformation reduces H to a power series in $\{(p^2+q^2)^n\}$ together with terms of higher order than ϵ^3, and so on.

$(n|H|n)$ can then be found from 5.3, or reduction formulae giving $\{(p^2+q^2)^n\}$ in terms of (p^2+q^2) can be built up (Table III). If terms beyond ϵ^2 can be neglected and if the terms of order ϵ in H are of order three or lower in p and q, $(n|H|n)$ can be written down immediately from Table V.

7. THE SLIGHTLY ANHARMONIC OSCILLATOR

If

$$
H=\left(\frac{1}{2m}p^2+\frac{1}{2}m\omega^2q^2\right)+\epsilon c_3q^3+\epsilon^2c_4q^4+\cdots, \tag{7.1}
$$

TABLE V. $H_1=H_1'+H_1''$, $[\tfrac{1}{2}(p^2+q^2), \{S'\}]=H_1'-H_1'^*$, $[\tfrac{1}{2}(p^2+q^2), H_1'^*]=0$, $\tfrac{1}{2}[\{S'\}, H_1''+H_1''^*]=C \sim D$

H_1'' \ H_1'	$\{q\}$	$\{p\}$	$\{q^2\}$	$\{qp\}$	$\{p^2\}$	$\{q^3\}$	$\{q^2p\}$	$\{qp^2\}$	$\{p^3\}$
$\{q\}$	$\{-\tfrac{1}{2}\}$ $-\tfrac{1}{2}$	0 0	$\{-\tfrac{1}{2}q\}$ 0	$\{-\tfrac{1}{2}p\}$ 0	$\{-\tfrac{1}{2}q\}$ 0	$\{-\tfrac{3}{2}q^2\}$ $-\tfrac{3}{4}(p^2+q^2)$	$\{-qp\}$ 0	$\{-\tfrac{1}{2}p^2\}$ $-\tfrac{1}{4}(p^2+q^2)$	0 0
$\{p\}$	0 0	$\{-\tfrac{1}{2}\}$ $-\tfrac{1}{2}$	$\{-\tfrac{1}{2}p\}$ 0	$\{-\tfrac{1}{2}q\}$ 0	$\{-\tfrac{1}{2}p\}$ 0	0 0	$\{-\tfrac{1}{2}q^2\}$ $-\tfrac{1}{4}(p^2+q^2)$	$\{-qp\}$ 0	$\{-\tfrac{3}{2}p^2\}$ $-\tfrac{3}{4}(p^2+q^2)$
$\{q^2\}$	$\{-\tfrac{1}{4}q\}$ 0	$\{\tfrac{1}{4}p\}$ 0	$\{-\tfrac{1}{2}q^2+\tfrac{1}{2}p^2\}$ 0	0 0	$\{-\tfrac{1}{2}q^2+\tfrac{1}{2}p^2\}$ 0	$\{-\tfrac{3}{4}q^3\}$ 0	$\{-\tfrac{1}{4}q^2p\}$ 0	$\{\tfrac{1}{4}qp^2\}$ 0	$\{\tfrac{3}{4}p^3\}$ 0
$\{qp\}$	$\{-\tfrac{1}{4}p\}$ 0	$\{-\tfrac{1}{4}q\}$ 0	$\{-\tfrac{1}{2}qp\}$ 0	$\{-\tfrac{1}{4}q^2-\tfrac{1}{4}p^2\}$ $-\tfrac{1}{4}(p^2+q^2)$	$\{-\tfrac{1}{2}qp\}$ 0	$\{-\tfrac{3}{4}q^2p\}$ 0	$\{-\tfrac{1}{4}q^3-\tfrac{1}{2}qp^2\}$ 0	$\{-\tfrac{1}{2}q^2p-\tfrac{1}{4}p^3\}$ 0	$\{-\tfrac{3}{4}qp^2\}$ 0
$\{p^2\}$	$\{\tfrac{1}{4}q\}$ 0	$\{-\tfrac{1}{4}p\}$ 0	$\{\tfrac{1}{2}q^2-\tfrac{1}{2}p^2\}$ 0	0 0	$\{\tfrac{1}{2}q^2-\tfrac{1}{2}p^2\}$ 0	$\{\tfrac{3}{4}q^3\}$ 0	$\{\tfrac{1}{4}q^2p\}$ 0	$\{-\tfrac{1}{4}qp^2\}$ 0	$\{-\tfrac{3}{4}p^3\}$ 0
$\{q^3\}$	$\{-\tfrac{1}{2}q^2-p^2\}$ $-\tfrac{3}{4}(p^2+q^2)$	$\{qp\}$ 0	$\{-\tfrac{1}{2}q^3\}$ 0	$\{\tfrac{1}{2}q^2p-p^3\}$ 0	$\{-\tfrac{1}{2}q^3\}$ 0	$\{-\tfrac{3}{2}q^4-3q^2p^2+\tfrac{1}{2}\}$ $-\tfrac{15}{16}(p^2+q^2)^2-\tfrac{7}{16}$	$\{-2qp^3\}$ 0	$\{\tfrac{3}{2}q^2p^2+\tfrac{1}{4}-p^4\}$ $-\tfrac{3}{16}(p^2+q^2)^2+\tfrac{5}{16}$	$\{3qp^3\}$ 0
$\{q^2p\}$	0 0	$\{-\tfrac{1}{2}q^2\}$ $-\tfrac{1}{4}(p^2+q^2)$	$\{-\tfrac{1}{2}q^2p\}$ 0	$\{-\tfrac{1}{2}q^3\}$ 0	$\{-\tfrac{1}{2}q^2p\}$ 0	0 0	$\{-\tfrac{1}{2}q^4\}$ $-\tfrac{3}{16}(p^2+q^2)^2-\tfrac{3}{16}$	$\{-q^3p\}$ 0	$\{-\tfrac{3}{2}q^2p^2+\tfrac{1}{4}\}$ $-\tfrac{3}{16}(p^2+q^2)^2+\tfrac{1}{16}$
$\{qp^2\}$	$\{-\tfrac{1}{2}p^2\}$ $-\tfrac{1}{4}(p^2+q^2)$	0 0	$\{-\tfrac{1}{2}qp^2\}$ 0	$\{-\tfrac{1}{2}p^3\}$ 0	$\{-\tfrac{1}{2}qp^2\}$ 0	$\{-\tfrac{3}{2}q^2p^2+\tfrac{1}{4}\}$ $-\tfrac{3}{16}(p^2+q^2)^2+\tfrac{1}{16}$	$\{-qp^3\}$ 0	$\{-\tfrac{1}{2}p^4\}$ $-\tfrac{3}{16}(p^2+q^2)^2-\tfrac{3}{16}$	0 0
$\{p^3\}$	$\{qp\}$ 0	$\{-q^2-\tfrac{1}{2}p^2\}$ $-\tfrac{3}{4}(p^2+q^2)$	$\{-\tfrac{1}{2}p^3\}$ 0	$\{-q^3+\tfrac{1}{2}qp^2\}$ 0	$\{-\tfrac{1}{2}p^3\}$ 0	$\{3q^3p\}$ 0	$\{-q^4+\tfrac{3}{2}q^2p^2+\tfrac{1}{4}\}$ $-\tfrac{3}{16}(p^2+q^2)^2+\tfrac{5}{16}$	$\{-2q^3p\}$ 0	$\{-3q^2p^2+\tfrac{1}{2}-\tfrac{3}{2}p^4\}$ $-\tfrac{3}{16}(p^2+q^2)^2-\tfrac{3}{16}$

Replace p by $p/\sqrt{(m\hbar\omega)}$, q by $q/\sqrt{(m\omega/h)}$, H by $H/\hbar\omega$, S by $S/\hbar$.

where

$$qp-pq=i\hbar \tag{4.1}$$

transformation with

$$S=\epsilon c_3\left\{\frac{p^*q^{*2}}{m\omega^2}+\frac{2}{3}\frac{p^{*3}}{m^3\omega^4}\right\} \qquad \text{(Table IV)} \tag{7.2}$$

gives to order ϵ^2

$$H^*=\left\{\frac{1}{2m}p^{*2}+\frac{1}{2}m\omega^2q^{*2}+\epsilon^2\left(\left(c_4-\frac{3}{2}\frac{c_3^2}{m\omega^2}\right)q^{*4}-\frac{3c_3^2}{m^3\omega^4}p^{*2}q^{*2}+\frac{\hbar^2c_3^2}{2m^3\omega^4}\right)+\cdots\right\}, \qquad \text{(Table V)} \tag{7.3}$$

which a further transformation reduces to

$$H^{**}=\hbar\omega\left(\frac{1}{2m\hbar\omega}p^{**2}+\frac{1}{2}\frac{m\omega}{\hbar}q^{**2}\right)$$
$$+\epsilon^2\left(\left(\frac{3}{8}\frac{c_4}{m^2\omega^2}-\frac{15}{16}\frac{c_3^2}{m^3\omega^4}\right)\left(\left(\frac{1}{m\omega}p^{**2}+m\omega q^{**2}\right)^2+\hbar^2\right)+\frac{\hbar^2c_3^2}{2m^3\omega^4}\right) \qquad \text{(Tables III, V)} \tag{7.4}$$

giving for the nth state, since

$$\frac{1}{2m\hbar\omega}p^{**2}+\frac{1}{2}\frac{m\omega}{\hbar}q^{**2}=n+\tfrac{1}{2},$$

$$E_n=(n+\tfrac{1}{2})\hbar\omega+\frac{\epsilon^2\hbar^2}{m^2\omega^2}\left(\tfrac{3}{2}c_4(n^2+n+\tfrac{1}{2})-\frac{c_3^2}{m\omega^2}\left(\frac{30n^2+30n+11}{8}\right)\right)+\cdots \tag{7.5}$$

Further, if

$$\mathbf{e}=\mathbf{e}_0+\epsilon\mathbf{e}_1q+\epsilon^2\mathbf{e}_2q^2+\cdots, \tag{7.6}$$

transformation with 7.2 gives

$$\mathbf{e}=\mathbf{e}^*(p^*, q^*)=\mathbf{e}_0+\epsilon\mathbf{e}_1q^*+\epsilon^2\left(\mathbf{e}_2q^{*2}-c_3\mathbf{e}_1\left(\frac{q^{*2}}{m\omega^2}+2\frac{p^{*2}}{m^3\omega^4}\right)\right)+\cdots \qquad \text{(Table II).} \tag{7.7}$$

To this order the further transformation makes no change, and the matrix components of **e** in a system in which H is diagonal can be written down at once.[7]

8. DUNHAM'S RESULTS

To obtain the terms of the next two orders in E for the anharmonic oscillator, Dunham's[8] results, Table II (formula 4.5) were extended to cover $[\{A\},\{B\}]=\{C\}$ up to terms of order q^8 in C. If

$$H=\tfrac{1}{2}p^2+\tfrac{1}{2}q^2+aq^3+bq^4+cq^5+dq^6+eq^7+fq^8+\cdots, \tag{8.01}$$

where

$$qp-pq=i, \tag{8.02}$$

transformation with

$$S=a\{pq^2+\tfrac{2}{3}p^3\} \qquad \text{(Table IV)} \tag{8.03}$$

removes aq^3 giving by 3.51, 3.52, $\cdots$ and using Table II repeatedly,

$$\begin{aligned}H=\{&\tfrac{1}{2}(q^2+p^2)+bq^4+\tfrac{1}{2}a^2(-3q^4-6q^2p^2+1)+cq^5+ab(-4q^5-8q^3p^2+4q)\\&+\tfrac{1}{3}a^3(12q^5+12q^3p^2-18q+24qp^4)+dq^6+ac(-5q^6-10q^4p^2+10q^2)+\tfrac{1}{2}a^2b(20q^6+32q^4p^2\\&-56q^2+48q^2p^4-16p^2)+\tfrac{1}{8}a^4(-60q^6-108q^4p^2+156q^2+96q^2p^4+120p^2-48p^6)+eq^7\\&+ad(-6q^7-12q^5p^2+20q^3)+\tfrac{1}{2}a^2c(30q^7+60q^5p^2-140q^3+80q^3p^4-80qp^2)\\&+\tfrac{1}{6}a^3b(-120q^7-240q^5p^2+576q^3+32q^3p^4+576qp^2-192qp^6)+\tfrac{1}{30}a^5(360q^7+720q^5p^2\\&-1728q^3+1440q^3p^4-960qp^6)+fq^8+ae(-7q^8-14q^6p^2+35q^4)+\tfrac{1}{2}a^2d(42q^8+96q^6p^2\\&-300q^4+120q^4p^4-240q^2p^2+20)+\tfrac{1}{6}a^3c(-210q^8-480q^6p^2+1620q^4-200q^4p^4+1920q^2p^2\\&-180-480q^2p^6+240p^4)+\tfrac{1}{24}a^4b(840q^8+1920q^6p^2-6528q^4+2560q^4p^4-3840q^2p^2+864\\&-2304q^2p^6-2560p^4+384p^8)+\tfrac{1}{144}a^6(-2520q^8-5760q^6p^2+19584q^4+30528q^2p^2-1728\\&-19200q^2p^6-5760p^4+1920p^8)+\cdots\}.\end{aligned} \tag{8.04}$$

A second transformation with

$$\begin{aligned}S=\{&b(\tfrac{5}{8}q^3p+\tfrac{3}{8}qp^3)+\tfrac{1}{2}a^2(-\tfrac{9}{8}q^3p-\tfrac{15}{8}qp^3)+c(q^4p+\tfrac{4}{3}q^2p^3+\tfrac{8}{15}p^5)\\&+ab(-4q^4p-8q^2p^3-\tfrac{16}{5}p^5+4p)+\tfrac{1}{3}a^3(12q^4p+20q^2p^3+\tfrac{64}{5}p^5-18p)\}\end{aligned} \qquad \text{(Table IV)} \tag{8.05}$$

reduces

$$\{bq^4+\tfrac{1}{2}a^2(-3q^4-6q^2p^2+1)+cq^5+ab(-4q^5-8q^3p^2+4q)+\tfrac{1}{3}a^3(12q^5+12q^3p^2-18q+24qp^4)\}$$

to

$$\{\tfrac{3}{8}b(q^2+p^2)^2+\tfrac{1}{16}a^2(-15(q^2+p^2)^2+8)\},$$

giving, by 3.51, 3.52, $\cdots$, and using Table II repeatedly,

$$\begin{aligned}H=\{&\tfrac{1}{2}(q^2+p^2)+\tfrac{3}{8}b(q^2+p^2)^2+\tfrac{1}{16}a^2(-15(q^2+p^2)^2+8)+dq^6+ac(-5q^6-10q^4p^2+10q^2)\\&+\tfrac{1}{32}a^2b(467q^6+713q^4p^2-1274q^2+777q^2p^4-58p^2-45p^6)+\tfrac{1}{128}a^4(-1311q^6-2781q^4p^2\\&+3900q^2+771q^2p^4+840p^2-543p^6)+\tfrac{1}{32}b^2(-55q^6-69q^4p^2+72q^2+27q^2p^4-36p^2+9p^6)+eq^7\\&+ad(-6q^7-12q^5p^2+20q^3)+a^2c\tfrac{1}{32}(681q^7+1341q^5p^2-3245q^3+1664q^3p^4-1856qp^2\\&+256qp^6)+a^3b\tfrac{1}{24}(-1497q^7-4161q^5p^2+8247q^3-3296q^3p^4+9210qp^2-2028qp^6)\end{aligned}$$

[7] M. Born and P. Jordan, Zeits. f. Physik **34**, 858 (1925).
[8] J. L. Dunham, Phys. Rev. **41**, 713, 721 (1932).

$$
\begin{aligned}
&+a^5\tfrac{1}{80}(2970q^7+7020q^5p^2-18318q^3+11430q^3p^4-19890qp^2+3460qp^6)\\
&+bc\tfrac{1}{48}(-207q^7-555q^5p^2+507q^3-256q^3p^4+768qp^2)+ab^2\tfrac{1}{4}(69q^7+243q^5p^2-307q^3\\
&+194q^3p^4-396qp^2)+fq^8+ae(-7q^8-14q^6p^2+35q^4)+\tfrac{1}{4}bd(-15q^8-27q^6p^2+45q^4)\\
&+\tfrac{1}{6}c^2(-15q^8-60q^6p^2+60q^4-40q^4p^4+240q^2p^2-12)+\tfrac{1}{8}a^2d(195q^8+519q^6p^2-1425q^4\\
&+480q^4p^4-960q^2p^2+80)+\tfrac{1}{12}abc(465q^8+1215q^6p^2-3051q^5+1570q^4p^4-3858q^2p^2\\
&+288+384q^2p^6-448p^4)+\tfrac{1}{128}b^3(425q^8+620q^6p^2-2310q^4+930q^4p^4+612q^2p^2+108q^2p^4\\
&-342p^4+27p^8)+\tfrac{1}{24}a^3c(-1725q^8-5595q^6p^2+13959q^4-3850q^4p^4+16794q^2p^2-1488\\
&-1664q^2p^6+2688p^4-256p^8)+\tfrac{1}{256}a^2b^2(-23125q^8-60116q^6p^2+185450q^4-65150q^4p^4\\
&+2080740q^2p^2-20480-55380q^3p^6+45242p^4-405p^8)+\tfrac{1}{3072}a^4b(586614q^8+1927128q^6p^2\\
&-5241036q^4+1897540q^2p^4-6127800q^2p^2+700416+246744q^2p^6-1905004p^4+216438p^8)\\
&+\tfrac{1}{1024}a^6(-89903q^8-339260q^6p^2+841278q^4-259930q^4p^4+1210284q^2p^2-131072\\
&\qquad\qquad-59324q^2p^6+358574p^4-42543p^8)+\cdots\}. \qquad (8.06)
\end{aligned}
$$

A further transformation removes the terms of the order of eq^7 and gq^9 and reduces H to the form (Table III)

$$
\begin{aligned}
H=\;&\tfrac{1}{2}(q^2+p^2)+\tfrac{1}{8}b(3(q^2+p^2)^2+3)+\tfrac{1}{16}a^2(-15(q^2+p^2)^2-7)+\tfrac{1}{16}d(5(q^2+p^2)^3+25(q^2+p^2))\\
&+\tfrac{1}{16}ac(-35(q^2+p^2)^3-95(q^2+p^2))+\tfrac{1}{32}a^2b(225(q^2+p^2)^3+459(q^3+p^2))\\
&+\tfrac{1}{128}a^4(-705(q^2+p^2)^3-1155(q^2+p^2))+\tfrac{1}{32}b^2(-17(q^2+p^2)^3-67(q^2+p^2))\\
&+\tfrac{1}{128}f(35(q^2+p^2)^4+490(q^2+p^2)^2+315)+\tfrac{1}{128}ae(-315(q^2+p^2)^4-2730(q^2+p^2)^2-1155)\\
&+\tfrac{1}{128}bd(-165(q^2+p^2)^4-1770(q^2+p^3)^3-945)+\tfrac{1}{256}c^2(-315(q^2+p^2)^4-2170(q^2+p^2)^2\\
&-1107)+\tfrac{1}{256}a^2d(2715(q^2+p^2)^4+17070(q^2+p^2)^2+6055)+\tfrac{1}{128}abc(2415(q^2+p^2)^4\\
&+14670(q^2+p^2)^2+5667)+\tfrac{1}{256}b^3(6000(q^2+p^2)^4+13656(q^2+p^2)^2+1539)\\
&+\tfrac{1}{256}a^3c(-9765(q^2+p^2)^4-47730(q^2+p^2)^2-14777)+\tfrac{1}{512}a^2b^2(-24945(q^2+p^2)^4\\
&-248052(q^2+p^2)^2-40261)+\tfrac{1}{1024}a^4b(116325(q^2+p^2)^4+479970(q^2+p^2)^2+131817)\\
&+\tfrac{1}{2048}a^6(-115755(q^2+p^2)^4-418110(q^2+p^2)^2-101479)+\text{terms of order }a^8. \qquad (8.07)
\end{aligned}
$$

This result agrees with that of Dunham by the W. K. B. method;[8] the terms $\tfrac{1}{128}f\,315-\tfrac{1}{128}\,ae\,1155-\tfrac{1}{128}\,bd\,945-\cdots-\tfrac{1}{2048}\,a^6\,101479$, not given by Dunham, check with an independent calculation by Dunham's method. The method used here may be regarded as differing from that of Dunham essentially only by expanding the potential energy in a power series first, and then expanding the transformation in powers of $\hbar$, while the W. K. B. method expands in powers of $\hbar$ first and Dunham expands the potential energy later. Except for the terms not given by Dunham, his method obtains the form for H more briefly than this method; but these terms, the only ones of order $\hbar^2$, require in his method nearly as much time as all the rest; in this method they are obtained with the others. We see also that, while for perturbation theory we require only the infinitesimal classical contact transformations, if we tried to determine the finite contact transformation corresponding to an arbitrary potential energy $V(q)$ we should be led back to the phase-integral and for the quantum theory corrections to the W. K. B. method.