Unitary Operators and Variational Approaches for One-Dimensional Hamiltonians

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Several variational approaches for the one-dimensional Schrödinger equation are devised by recourse to suitable expansions of the unitary operator that relates the corresponding eigenstates of the harmonic oscillator. A connection with the virial theorem, via scaling properties is established and an application to the ring puckering motion is discussed.

§ 1. Introduction

In a recent study,[1] an approximate, variational method for dealing with the *ground state* of Hamiltonians of the form

$$\hat{H} = \hat{H}_0 + \hat{V} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \lambda V(\hat{x}) \tag{1·1}$$

has been presented, $V(x)$ representing a broad class of even functions of the coordinate ($V(x) \in C^\infty$), which admit a series expansion. The idea of the method is that of relating the eigenstates of H to those of H_0 via a unitary operator $\exp(iF)$ to be determined by recourse to the variational principle.

The method presented in Ref. 1) exhibits two features that make it a very convenient one for practical applications, namely i) it is an extremely simple one from the numerical point of view and no integrals involving $V(x)$ are to be faced and ii) it allows one to deal, in a very simple way, with the whole unperturbed basis, without truncating it. However, the method yields a rigorous upper bound to those eigenvalues of H corresponding to the ground state (g.s.) and the first excited state only (as shown in Ref. 1), these are very good upper bounds indeed). Consequently, its use for other excited states cannot be justified.

A first order approximation to F has been extensively investigated in Ref. 1). In the present work, we wish to pursue that investigation in order to extend the scope of the corresponding formalism.

First of all, we will show that the first order treatment involved in Ref. 1) is tantamount to a scaling of the corresponding wavefunction. If the relevant scaling parameter is now determined by recourse to the variational principle, this will be seen to lead one in a natural fashion to the virial theorem, which in turn will allow for an extension of the approach to excited states. Further, the introduction of higher order terms in the F-expansion will permit one to obtain sensible improvements to the upper bounds (for the g.s. and the first excited state) that the method provides.

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§ 2.　Scaling and mapping operator

We assume that $V(x)$ in $(1\cdot1)$ admits a series expansion of the form

$$V(x)=\sum_{j=0}^{\infty}\frac{V^{(j)}(c)}{j!}(x-c)^{j} \qquad (2\cdot1)$$

and set for simplicity $c=0$.　In appropriate units, our problem is then that of looking for the spectrum of the differential operator

$$-\frac{d^2}{dx^2}+x^2+\sum_{j=0}^{\infty}\frac{V^{(j)}(0)}{j!}x^{j} . \qquad (2\cdot2)$$

A variational approximation which yields a rigorous upper bound to the two lower eigenvalues of $(2\cdot2)$ is developed in Ref. 1) as follows:　One first introduces the creation and destruction operators

$$\hat{a}^{\dagger}=\hat{p}+i\hat{x} , \qquad \hat{a}=\hat{p}-i\hat{x} \qquad (2\cdot3)$$

so that

$$[\hat{a}, \hat{a}^{\dagger}]=2 \qquad (2\cdot4)$$

and then, after rewriting H as

$$\hat{H}=\hat{H}_0+\sum_{j=0}\lambda_j\hat{B}^{j} \qquad (2\cdot5)$$

with

$$\hat{B}=-i(\hat{a}^{\dagger}-\hat{a}) ,$$
$$\hat{H}_0=\hat{a}^{\dagger}\hat{a}+1 \qquad (2\cdot6)$$

and

$$\lambda_j=\lambda\frac{V^{(j)}(0)}{j! \ 2^{j}} \qquad (2\cdot7)$$

one relates the eigenstates j of H_0 to those J of H by means of a mapping operator

$$|J\rangle=\exp(i\hat{F}^{(j)})|j\rangle \qquad (2\cdot8)$$

of the general form

$$\hat{F}^{(j)}=i\sum_{k=1}^{\infty}h_k^{(j)}(\hat{a}^{\dagger 2k}-\hat{a}^{2k})=\sum_{k=1}^{\infty}\hat{F}_k^{(j)} . \qquad (2\cdot9)$$

Minimization of $\langle 0|H|0\rangle$ (g.s.) or $\langle 1|H|1\rangle$ (first excited state) with respect to the quantities $h_k^{(0)}$ or $h_k^{(1)}$ of $(2\cdot9)$ would lead to the exact solution.　The supraindexes j in $(2\cdot8)$ and $(2\cdot9)$ explicitly remind us of the fact that, for each eigenstate J one wishes to deal with, a different set of parameters $h_k^{(j)}$ is needed.　For the sake of a simpler notation, these supraindexes will be omitted henceforth.　A good *approximation*[1] is that of retaining only the first term and employ a mapping operator defined by

$$\widehat{F}_1 = ih_1(\widehat{a}^{\dagger 2} - \widehat{a}^2) \tag{2.10}$$

which contains just one variational parameter h. One obtains an upper bound to either the g.s. or the first excited state by minimization with respect to this variational parameter. The corresponding expression is[1)]

$$E_j(h) = (2j+1)\cosh(8h) + \widehat{P}_j(\widehat{k})\phi(h), \tag{2.11}$$

where the operators $\widehat{P}$ and $\widehat{k}$ are defined by

$$\widehat{k} = \frac{1}{8}\frac{d}{dh} \tag{2.12}$$

and

$$\widehat{P}_j(\widehat{k}) = \sum_{p=0} 2^{j-p}\binom{\widehat{k}}{j-p}\binom{j}{p}. \tag{2.13}$$

The function $\phi(h)$ is related to $V(x)$ by

$$\phi(h) = \frac{e^{-4h}}{\pi^{1/2}}f_V(e^{-8h}), \tag{2.14}$$

$f_V(z)$ denoting the Laplace transform of $V(x^{1/2})/x^{1/2}$.

Formally, one obtains an expression of the type (2.11) for any value of j. As discussed in Ref. 1), only for $j=0$ is the corresponding procedure a legitimate one, since for $j \geq 1$, E_j does not provide us with an upper bound to the corresponding eigenvalue of H.

Before going any further, we first examine an interesting property of the operator $\widehat{F}_1$, given by (2.10). Written in terms of $\widehat{x}$ and $\widehat{p}$, $\widehat{F}_1$ is proportional to the so-called correlation operator $\widehat{L}$

$$\widehat{L} = \widehat{x}\widehat{p} + \widehat{p}\widehat{x} \tag{2.15}$$

i.e.,

$$\widehat{F}_1 = -2h\widehat{L} \tag{2.16}$$

and easily finds that the mapping operator $\exp(i\widehat{F})$ possesses the following property,

$$\exp(i\widehat{F})f(x) = \exp(-2h\widehat{L})f(x) = \exp(-2h)f(\exp(-4h)x). \tag{2.17}$$

In other words, our first order mapping operator (2.10) is a scaling operator, the scaling parameter being $\beta = \exp(-4h)$. If we define

$$\widehat{S}(\beta) = \exp(i\widehat{F}_1(h)), \qquad \beta > 0 \tag{2.18}$$

we see that Eq. (2.17) adopts the appearance

$$\widehat{S}(\beta)f(x) = \beta^{1/2}f(\beta x) \tag{2.19}$$

which neatly displays the scaling character of $\widehat{S}$.

It is well known that an energy minimization with respect to a scaling parameter is tantamount to complying with the prescriptions of the virial theorem. Consequent-

ly, this fact can now be legitimately invoked in order to extend the applications of the approach of Ref. 1) to the calculation of excited states, although only for $j=0, 1$ the corresponding approximate energies can be regarded as upper bounds to the excited values.

§ 3.   Higher-order approximations

In order to investigate higher-order approximations to F, we start by writing the Hamiltonian in the general form (no harmonic x^2 term compulsorily included)

$$\hat{H}=-\frac{d^2}{dx^2}+V(\hat{x}) \tag{3·1}$$

with $V(x)$ subject to the same restrictions imposed before.   Equation (3·1) can be recasted as

$$\hat{H}=\frac{1}{4}(\hat{a}^{\dagger 2}+\hat{a}^2+2\hat{a}^{\dagger}\hat{a}+2)+\sum_{j=0}\frac{V^{(2j)}(0)}{(2j)!}\frac{\hat{B}^{2j}}{2^{2j}}. \tag{3·2}$$

The other essential ingredient here, namely the operator $\hat{F}$, can be written in the form of a series, whose terms have the appearance

$$\hat{F}_k=ih_k(\hat{a}^{\dagger 2k}-\hat{a}^{2k})=ih_k\hat{A}_k \tag{3·3}$$

with a commutation relation given by (for $n<m$)

$$[\hat{F}_n,\hat{F}_m]=h_nh_m\sum_{k=1}^{2n}\binom{2n}{k}\binom{2m}{k}k!(\hat{a}^{\dagger 2m-k}\hat{a}^{2n-k}-\hat{a}^{\dagger 2n-k}\hat{a}^{2m-k}). \tag{3·4}$$

As the $\hat{F}_k$ do not (in general) commute, going to higher orders in the $\hat{F}$-expansion makes matters much more complicated than in the first order situation.   A slight modification to the ideas of § 2 becomes necessary in order to make things a bit simpler.   The central idea is that of relating the eigenstate $|J\rangle$ of $\hat{H}$ to the corresponding one $|j\rangle$ of $\hat{H}_0(\hat{H}=\hat{H}_0+V(\hat{x})-\hat{x}^2)$ by means of a unitary transformation, effected by the operator $\hat{T}$:

$$|J\rangle=\hat{T}|j\rangle, \tag{3·5}$$

$$\hat{T}=\prod_{k=1}^{\infty}\exp(i\hat{F}_k)=\prod_{k=1}^{\infty}\exp(-h_k\hat{A}_k). \tag{3·6}$$

The h_k being determined by minimizing

$$E_j(\boldsymbol{h})=\langle j|\hat{T}^{\dagger}\hat{H}\hat{T}|j\rangle \tag{3·7}$$

with respect to the "vector" $\boldsymbol{h}$ of components $h_1, h_2, \cdots$.
    Notice that if the $\hat{F}$ do commute among themselves we fall back upon the method developed in § 2.   Of course, (3·6) presents us with a transformation as general as the one given by (2·8), being neither a superior nor an inferior one.
    We build now the following hierarchy of operators,

$$\hat{H}_1(h_1) = \exp(h_1 \hat{A}_1)\hat{H}\exp(-h_1\hat{A}_1),$$

$$\hat{H}_2(h_1, h_2) = \exp(h_2\hat{A}_2)\hat{H}_1(h_1)\exp(-h_2\hat{A}_2),$$

$$\vdots$$

$$\hat{H}_N(\boldsymbol{h}_N) = \exp(h_N\hat{A}_N)\hat{H}_{N-1}(\boldsymbol{h}_{N-1})\exp(-h_N\hat{A}_N). \tag{3·8}$$

The first operator is immediately obtained by recourse to Eqs. (2·17~19), employing the scaling property previously discussed (we continue calling the scaling variable β)

$$\hat{H}_1(\beta) = \hat{S}(\beta)\hat{H}(\hat{p}, \hat{x})\hat{S}(\beta) = \hat{H}(\beta\hat{p}, \hat{x}/\beta). \tag{3·9}$$

For the Hamiltonian (3·2) we thus write

$$\hat{H}_1(\beta) = \frac{\beta^2}{4}(\hat{a}^{\dagger 2} + \hat{a}^2 + 2\hat{a}^\dagger\hat{a} + 2) + \sum_{k=0}\frac{V^{(2k)}(0)}{(2k)!\,2^{2k}}\left(\frac{\hat{B}}{\beta}\right)^{2k} \tag{3·10}$$

which can be conveniently written by a suitable ordering of the operators $\hat{a}^\dagger$ and $\hat{a}$ as

$$\hat{H}_1(\beta) = \sum_{rs} H_{rs}^{(1)}\hat{a}^{\dagger r}\hat{a}^s, \tag{3·11}$$

where the $H_{rs}^{(N)}$-coefficients depend upon β. They are readily evaluated according to (3·10). The general operator H_N is of the form

$$\hat{H}_N(\beta, \boldsymbol{h}) = \sum_{rs} H_{rs}^{(N)}\hat{a}^{\dagger r}\hat{a}^s, \tag{3·12}$$

and, in order to obtain $H_{rs}^{(N)}(\beta, \boldsymbol{h})$, a recurrence algorithm is to be employed. Thus, if we introduce still another set of operators

$$\hat{C}^{(2,0)} = \hat{H}_1(\beta),$$

$$\hat{C}^{(2,n+1)} = [\hat{A}_2, \hat{C}^{(2,n)}], \tag{3·13a}$$

we can write

$$\hat{H}_2(\beta, h_2) = \sum_n \frac{h_2^n}{n!}\hat{C}^{(2,n)}, \tag{3·14a}$$

and, in similar fashion,

$$\hat{C}^{(N,0)} = \hat{H}_{N-1},$$

$$\hat{C}^{(N,n+1)} = [\hat{A}_N, \hat{C}^{(N,n)}], \tag{3·13b}$$

$$\hat{H}_N = \sum_n \frac{h_N^n}{n!}\hat{C}^{(N,n)}. \tag{3·14b}$$

In order to evaluate the $\hat{C}^{(N,n)}$ we employ the "ordered" expansions introduced with Eq. (3·11)

$$\hat{C}^{(N,n)} = \sum_{rs} c_{rs}^{(N,n)}\hat{a}^{\dagger r}\hat{a}^s \tag{3·15}$$

and determine the coefficients in (3·15) according to

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$$c_{rs}^{(N,n+1)} = -(2N)! \sum_{k=1}^{2N} \frac{2^k}{(2N-k)!\,k!} \left(t_{sk} c_{r+k-2N,s+k}^{(N,n)} + t_{rk} c_{r+k,s+k-2n}^{(N,n)} \right), \qquad (3\cdot16)$$

where

$$t_{vk} = \frac{(k+v)!}{v!}$$

so that

$$H_{rs}^{(N)} = \sum_n \frac{h_N}{n!} c_{rs}^{(N,n)} \qquad (3\cdot17)$$

and

$$\widehat{H}_N = \sum_{rs} \widehat{a}^{\dagger r} \widehat{a}^s \sum_n \frac{h_N}{n!} c_{rs}^{(N,n)}. \qquad (3\cdot18)$$

Finally, using

$$\langle j | \widehat{a}^{\dagger r} \widehat{a}^s | j \rangle = 2^r r! \binom{j}{r} \delta_{rs}, \qquad r < j \qquad (3\cdot19)$$

we arrive at

$$E_j^{(N)}(\beta, \boldsymbol{h}) = \langle j | \widehat{H}_N | j \rangle = \sum_n \frac{h_N}{n!} \sum_{r=0}^j 2^r r! \binom{j}{r} c_{rr}^{(N,n)}, \qquad (3\cdot20)$$

and, in particular,

$$E_0^{(N)} = \sum_n \frac{h_N^{\,n}}{n!} c_{00}^{(N,n)},$$

$$E_1^{(N)} = \sum_n \frac{h_N^{\,n}}{n!} \left(c_{00}^{(N,n)} + 2 c_{11}^{(N,n)} \right). \qquad (3\cdot21)$$

In $(3\cdot20)$ we have N-parameters $(\beta, h_2, h_3, \cdots, h_N)$, which are to be fixed by a minimization procedure.

An alternative approach that may be easier to implement would run as follows: evaluate first

$$\varepsilon_j^{(1)}(\beta) = \langle j | \widehat{H}_1(\beta) | j \rangle \qquad (3\cdot22)$$

and minimize this with respect to β. Once β is fixed, proceed to

$$\varepsilon_j^{(2)}(h_2) = \langle j | H_2(h_2) | j \rangle \qquad (3\cdot23)$$

and minimize it with respect to h_2. The algorithm continues with $\varepsilon_j^{(3)}(h_3)$ and so on.

§ 4. Application

During the past few years there has been quite an interest in the nature of the low-lying frequency ring-puckering motion in four membered rings, as, for instance,

in the case of the trimethilene oxide molecule (see Refs. 2)~4) and references therein). The nature of the vibration depends on the potential function governing the mode, which in turn depends on the relative magnitudes of two opposing forces on the molecule. One of them (the ring strain) tends to make it planar since puckering ring further decreases the already highly strained ring angles and thus increases the potential energy of the molecule. Opposing the ring strain we have the barrier to internal rotation, which results in a torsional force about the ring bonds and tends to make the ring attain a puckered configuration. These two competing forces are rather large, the final configuration of the molecule representing a delicate balance between them. When the torsional force dominates, the potential function will have a double minimum with a barrier to the planar configuration.

Abundant experimental evidence suggests representing the corresponding potential function by (in appropriate units)

$$V(x) = -x^2 + \lambda x^4 \qquad (4\cdot1)$$

x denoting the out-of-plane vibrational displacement of the ring atoms from the hypothetical average plane defined by the planar ring.

We will apply our method within the present context for a wide range of λ-values. The scaled Hamiltonian reads

$$\hat{H}_1(\beta) = A_{20}(\hat{a}^{\dagger 2} + \hat{a}^2) + A_{11}\hat{a}^\dagger \hat{a} + A_{40}(\hat{a}^{\dagger 4} + \hat{a}^4) + A_{31}(\hat{a}^{\dagger 3}\hat{a} + \hat{a}^\dagger \hat{a}^3)$$

$$+ A_{22}(\hat{a}^{\dagger 2}\hat{a}^2) + A_{00}, \qquad (4\cdot2)$$

where

$$A_{20} = \frac{\beta^2}{4} + \frac{1}{4\beta^2} - \frac{12\lambda}{(2\beta)^4},$$

$$A_{11} = \frac{\beta^2}{4} - \frac{1}{2\beta^2} + \frac{24\lambda}{(2\beta)^4},$$

$$A_{40} = \frac{\lambda}{(2\beta)^4},$$

$$A_{31} = -\frac{4\lambda}{(2\beta)^4},$$

$$A_{22} = \frac{6\lambda}{(2\beta)^4},$$

$$A_{00} = \frac{\beta^2}{2} - \frac{1}{2\beta^2} + \frac{12\lambda}{(2\beta)^4}. \qquad (4\cdot3)$$

Energy values corresponding to the g.s. and to the first nine excited levels of our Hamiltonian are tabulated in Table I. Several values of λ have been considered. For each value of λ two different figures are displayed. The upper one arises as a result of applying the $\exp(i\hat{F}_1)$ operator (cf. Eq. (3·22)), according to the methodology described in § 2. This number is to be compared to the best available result provided by current literature (see Ref. 5)), by recourse to a much more sophisticated treat-

ment, which is given in the second line.

The effect of higher order corrections to the treatment described in § 2 is exhibited in Table II with reference to higher order terms $\hat{F}_k$ $(k>2)$. One is able in this fashion to obtain, for the ground state and first excited state, better upper bounds than the ones provided by the $\exp(i\hat{F})$ approach, as evidenced by the energy values tabulated there.

Table I. Energy values corresponding to the ground state (E_0) and to the first nine excited levels of the Hamiltonian (4·2). In each instance the value obtained with the $\exp(i\hat{F}_1)$ approximation of § 2 (upper figure) is compared to that of Ref. 5) (lower figure).

	E_0	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9
0.5	0.3556	1.8354	4.1974	7.0687	10.3210	13.8850	17.7170	21.787	26.0710	30.5500
	0.2945	1.7445	4.2559	7.1822	10.4903	14.1089	17.9974	22.1233	26.4649	31.0084
1.0	0.7040	2.9162	6.1198	9.9293	14.1990	18.8491	23.828	29.0970	34.6300	40.4040
	0.6576	2.8345	6.1639	10.0386	14.3726	19.0861	24.1314	29.4662	35.0879	40.9430
5.0	1.6412	6.0558	11.969	18.852	26.484	34.742	43.543	52.827	62.548	72.671
	1.5942	5.9582	12.012	18.992	26.721	35.077	43.979	53.368	63.198	73.438
10.0	2.1667	7.8768	15.432	24.193	33.890	44.368	55.526	67.289	79.601	92.416
	2.1129	7.7618	15.480	24.360	34.176	44.775	56.069	67.952	80.461	93.417
50.0	3.8903	13.935	27.055	42.207	58.942	77.002	92.216	116.457	137.630	159.660
	3.8074	13.752	27.128	42.476	59.410	77.671	97.124	117.555	139.092	161.231
100.0	4.9458	17.669	34.247	53.379	74.501	97.291	121.530	147.063	173.769	201.553
	4.8434	17.442	34.337	53.714	75.084	98.128	122.636	148.449	175.423	203.527

Table II. Energy values for the ground state and first excited state of the Hamiltonian of Table I as obtained by three different method, namely, $\exp(i\hat{F})$, $\exp(i\hat{F})$ (middle) and Ref. 5) (lowest) respectively.

	0.5	1.0	5.0	10.0	50.0	100.0
E_0	0.35563	0.70403	1.6412	2.1667	3.8903	4.9458
	0.31949	0.67211	1.6046	2.1240	3.8234	4.8628
	0.29447	0.65765	1.5942	2.1129	3.8074	4.8434
E_1	1.8354	2.9162	6.0558	7.8768	13.935	17.669
	1.7658	2.8497	5.9720	7.7772	13.775	17.470
	1.7445	2.8345	5.9582	7.7618	13.752	17.442

Table III. The energy values described in Table I as obtained by diagonalizing a 50×50 energy matrix in the harmonic oscillator basis. Underlined figures correspond to rather poor results.

	E_0	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9
0.5	0.29447	1.74452	4.25596	7.18218	10.4903	14.1087	17.9954	22.1201	26.4593	30.9951
1.0	0.65765	2.83453	6.16390	10.0386	14.3724	19.0857	24.1280	29.4628	35.0622	40.9040
5.0	1.59420	5.95820	12.0118	18.9917	26.7210	35.0778	43.9908	53.3905	63.2560	73.9957
10.0	2.11287	7.76181	15.4804	24.3604	34.1845	44.7984	56.1047	68.4323	84.2802	104.2150
50.0	3.80761	13.7582	27.1549	42.5405	60.8762	85.2925	125.5269	179.5811	269.4918	374.0165
100.0	4.8477	17.4678	34.4196	55.1555	86.1986	133.2087	215.9608	324.6260	506.5557	715.8055

Results of the same character as those of Table I are to be seen in Table III. Here, the corresponding energies arise as a result of a rather large (50×50) diagonalization of $\hat{H}$ in an optimized harmonic oscillator basis.

Acknowledgements

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