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Supersymmetric Quantum Mechanics, Excited State Energies and Wave Functions, and the Rayleigh−Ritz Variational Principle: A Proof of Principle Study[†]

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In addition to ground state wave functions and energies, excited states and their energies are also obtained in a standard Rayleigh−Ritz variational calculation. However, their accuracy is generally much lower. Using the super-symmetric (SUSY) form of quantum mechanics, we show that better accuracy and more rapid convergence can be obtained by taking advantage of calculations of the ground states of higher sector SUSY Hamiltonians, followed by application of the SUSY "charge operators". Our proof of principle study uses a general family of one-dimensional anharmonic oscillator models. We first obtain the exact, analytic ground states for a general family of anharmonic systems. We give the general, factorized form of the Hamiltonian for the hierarchy that arises in SUSY theory. The "charge" operators can then be used to convert states among the sectors. We illustrate the approach with two specific anharmonic oscillator models. Using the ground state of the second sector Hamiltonian, we show that the corresponding excited state energies and wave functions of the first sector are accurately obtained by applying the charge operators, using significantly smaller basis sets than are required in a standard variational approach applied to the original Schrödinger equation. This is a consequence of the higher accuracy of the Rayleigh−Ritz variational method when applied for ground states.

I. Introduction

The Rayleigh−Ritz variational method is a cornerstone of computational theoretical chemistry. However, it is well established that it delivers much better accuracy and convergence for ground state energies and wave functions, than for excited states.[1,2] In order to obtain similar accuracy for excited state energies, and specifically for excited state wave functions, one must endure a great deal of "overkill" for the ground state. It will be a significant advance if one can introduce a computational scheme which, at least to some degree, makes the computational effort required for excited state energies and wave functions more comparable to that of the ground state.

The approach we use to achieve this objective makes use of the super symmetric quantum mechanics (SUSY-QM) formulation. This approach grew out of an effort to generalize the ladder operator approach that is so powerful for the study of the harmonic oscillator. In fact, there is a long history of using ladder operator techniques for solving quantum mechanics problems (e.g., the harmonic oscillator, the hydrogen atom, angular momentum,[3−10] etc). The result of a systematic study of this approach to quantum mechanics led to the SUSY-QM approach.[11−15] In SUSY-QM, a "super-potential" is introduced, in terms of which the Hamiltonian can be factored, resulting in the SUSY generalization of the ladder operators (now called "charge operators"). More important for our study is the fact that one also obtains a hierarchy of Hamiltonians (called "sector" Hamiltonians) having the remarkable property of being isoenergetic with the spectrum of the original Hamiltonian (except for the original ground state). Thus, the ground state of the second sector Hamiltonian is degenerate with the first excited state of the original Hamiltonian. Even more important, the second sector ground state is also node-less, and there is every reason to expect that a Rayleigh−Ritz variational calculation of the second sector ground state energy also converges rapidly with high accuracy. Even more remarkably, one of the SUSY charge operators can then be used to convert the second sector ground state into the first excited state wave function. This should continue up the SUSY hierarchy of Hamiltonians.

The primary purpose of this paper, then, is to show that fundamental properties of SUSY-QM can be used to computational advantage for obtaining higher accuracy and more rapid convergence for excited state energies and wave functions, using the Rayleigh−Ritz variational method. This paper is organized as follows. In Section II, we present a brief introduction to SUSY-QM. In Section III, we formulate a general treatment of a family of anharmonic oscillators. In Section IV, we specialize to two specific examples of anharmonic oscillator models in order to illustrate the computational approach. In Section V we examine these systems computationally and compare the results of obtaining excited state wave functions and energies by Rayleigh−Ritz calculations of the ground states of the higher

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sector SUSY Hamiltonian, with the standard, variational QM approach to solutions for the original Hamiltonian. Finally, in Section VI we present our conclusions.

II. Introduction to the Hierarchical Hamiltonian Formulation of SUSY-QM

In SUSY-QM, one introduces operators that result in a factored Hamiltonian.[15] In certain cases, these correspond to raising (or "creation") and lowering (or "annihilation") operators, but in general, the charge operators transfer among sets of isospectral eigenstates. In fact, it is possible to develop a hierarchy of factored Hamiltonians (one for each excited bound state of the original system). It is this aspect of SUSY-QM that we shall take advantage of for a variational approach to determine accurate excited state energies and wave functions.

The general starting point is to define the so-called "superpotential", usually denoted as W. In the theory, W is related to the ground state wave function through the well-known Riccati substitution:[5]

$$\psi_0^1(x) = N\mathrm{e}^{-\int_0^x W(x')\mathrm{d}x'} \tag{II.1}$$

The relationship between the superpotential W and the physical interaction $V(x)$ results from assuming that eq II.1 solves the standard Schrödinger equation with energy zero. (This does not impose any restriction since the energy can be changed by adding any constant to the Hamiltonian.) Thus,

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_0^1}{\mathrm{d}x^2} + V_1\psi_0^1 = 0 \tag{II.2}$$

We easily see that

$$W_1 = -\frac{\frac{\mathrm{d}\psi_0^1}{\mathrm{d}x}}{\psi_0^1} = -\frac{\mathrm{d}}{\mathrm{d}x}\ln\psi_0^1 \tag{II.3}$$

It is readily verified that the Ricatti equation for W_1 is

$$-\frac{\hbar^2}{2m}\left[W_1^2(x) - \frac{\mathrm{d}W_1}{\mathrm{d}x}\right] + V_1 = 0 \tag{II.4}$$

and, if W_1 is known, V_1 is given by

$$V_1(x) = \frac{\hbar^2}{2m}\left(W_1^2(x) - \frac{\mathrm{d}W_1}{\mathrm{d}x}\right) \tag{II.5}$$

It is then evident that

$$-\frac{\mathrm{d}^2\psi_0^1}{\mathrm{d}x^2} + \left(W_1^2(x) - \frac{\mathrm{d}W_1}{\mathrm{d}x}\right)\psi_0^1 = 0 \tag{II.6}$$

However, the Hamiltonian operator now can be factored in the form

$$\begin{aligned}-\frac{\mathrm{d}^2}{\mathrm{d}x^2} + W_1^2(x) - \frac{\mathrm{d}W_1}{\mathrm{d}x} &= \\ \left[-\frac{\mathrm{d}}{\mathrm{d}x} + W_1(x)\right]&\left[\frac{\mathrm{d}}{\mathrm{d}x} + W_1(x)\right]\end{aligned} \tag{II.7}$$

We define the "charge" operator

$$Q_1 = \frac{\mathrm{d}}{\mathrm{d}x} + W_1 \tag{II.8}$$

and its adjoint is then given by (assuming W_1 is hermitian; i.e., ψ_0^1 is real)

$$Q_1^\dagger = -\frac{\mathrm{d}}{\mathrm{d}x} + W_1 \tag{II.9}$$

Then the "first sector" Hamiltonian is defined as

$$H_1 = Q_1^\dagger Q_1 \tag{II.10}$$

A "second sector" Hamiltonian is defined as

$$H_2 = Q_1 Q_1^\dagger \tag{II.11}$$

We note that, in principle, one might expect the ground state of H_2 to be given by

$$\psi_0^1(x) = N\mathrm{e}^{+\int_0^x W_1(x')\mathrm{d}x'}$$

For an unbounded domain, this will not be normalizable, since we already know that

$$\psi_0^1(x) = N\mathrm{e}^{-\int_0^z W_1(x')\mathrm{d}x'}$$

is L^2. The eigenspectra of H_1 and H_2 are positive semidefinite.

Let ψ_n^1 be an eigenstate of H_1 with energy $E_n \neq 0$. Then it follows that for $n > 0$, (since for $n = 0$, $E_0 = 0$),

$$Q_1^\dagger Q_1 \psi_n^1 = E_n^1 \psi_n^1 \tag{II.12}$$

We then apply Q_1 to the equation, to obtain

$$Q_1 Q_1^\dagger (Q_1 \psi_n^1) = E_n^1 Q_1 \psi_n^1 \tag{II.13}$$

Thus, $Q_1\psi_n^1$ is an eigenstate of H_2 with the same energy, E_n^1, as the state ψ_n^1. Similarly, consider the eigenstates of H_2:

$$H_2\psi_n^2 = Q_1 Q_1^\dagger \psi_n^2 = E_n^2 \psi_n^2 \tag{II.14}$$

Application of $Q^\dagger$, then implies that $Q_1^\dagger\psi_n^2$ is an eigenstate of H_1:

$$(Q_1^\dagger Q_1)(Q_1^\dagger \psi_n^2) = E_n^2 Q_1^\dagger \psi_n^2 \tag{II.15}$$

It follows that the Hamiltonians H_1 and H_2 have identical spectra (with the exception of the ground state, since the $E_0^1 = 0$ wave function is unique). In the case of the ground state ψ_0^1, we recall that

$$Q_1^\dagger Q_1 \psi_0^1 = 0 \tag{II.16}$$

which shows that the quantity

$$Q_1 \psi_0^1 \tag{II.17}$$

cannot be used to generate the ground state of the second sector. Indeed, eq II.16 indicates that such a ψ_0^2 would vanish identically.

Because of the uniqueness of the $E_0^1 = 0$ state, the indexing of the first and second sector levels must be modified. Consider

$$Q_1 Q_1^\dagger \psi_n^2 = E_n^2 \psi_n^2 \tag{II.18}$$

Then

$$Q_1^\dagger Q_1 (Q_1^\dagger \psi_{n+1}^1) = E_{n+1}^1 (Q_1^\dagger \psi_{n+1}^1) \tag{II.19}$$

since $Q\psi_0^1 \equiv 0$

So

$$E_n^2 = E_{n+1}^1 \tag{II.20}$$

and we conclude that

$$\psi_n^2 = \frac{Q_1 \psi_{n+1}^1}{\sqrt{E_{n+1}^1}} \tag{II.21}$$

and

$$\psi_{n+1}^1 = \frac{Q_1^\dagger \psi_n^2}{\sqrt{E_n^2}} \tag{II.22}$$

then

$$Q_1 \psi_{n+1}^1 = \sqrt{E_{n+1}^1} \psi_n^2 \tag{II.23}$$

From these expressions, it follows that

$$Q_1^\dagger Q_1 \psi_{n+1}^1 = \sqrt{E_{n+1}^1} Q^\dagger \psi_n^2 \tag{II.24}$$

$$= \sqrt{E_{n+1}^1} \sqrt{E_n^2} \psi_n^1 \tag{II.25}$$

$$= E_{n+1}^1 \psi_n^1 \tag{II.26}$$

which shows again that

$$E_{n+1}^1 = E_n^2 \tag{II.27}$$

The source of the degeneracy of H_1 and H_2 is the intertwining relation,

$$Q_1 H_1 = H_2 Q_1 \tag{II.28}$$

The next step in building a hierarchy of isospectral Hamiltonians is to define a second superpotential, W_2, according to

$$W_2 = -\frac{\mathrm{d}}{\mathrm{d}x} \ln \psi_0^2 \tag{II.29}$$

It is then clear that we can define an alternate form for H_2, given by

$$H_2 = Q_2^\dagger Q_2 + E_0^2 \tag{II.30}$$

where

$$Q_2 = \frac{\mathrm{d}}{\mathrm{d}x} + W_2 \tag{II.31}$$

We observe that ψ_0^2 is automatically an eigenstate of this form for H_2

$$H_2 \psi_0^2 = E_0^2 \psi_0^2 \tag{II.32}$$

since

$$Q_2 \psi_0^2 \equiv 0 \tag{II.33}$$

Next, consider the first excited state eigenvalue equation for the second sector:

$$H_2 \psi_1^2 = E_1^2 \psi_1^2 \tag{II.34}$$

We apply Q_2 to eq II.34 to find

$$(Q_2 Q_2^\dagger + E_0^2) Q_2 \psi_1^2 = E_n^2 Q_2 \psi_1^2 \tag{II.35}$$

Then, by similar reasoning, we deduce that

$$Q_2 \psi_1^2 = \sqrt{E_1^2 - E_0^2} \psi_0^3 \tag{II.36}$$

Using the new charge operators Q_2 and $Q_2^\dagger$, we then define the third sector Hamiltonian,

$$H_3 = Q_2 Q_2^\dagger + E_0^2 \tag{II.37}$$

with ground state equation

$$H_3 \psi_0^3 = E_0^3 \psi_0^3 \tag{II.38}$$

We then observe that by applying $Q_2^\dagger$ to eq II.38 gives

$$[(Q_2^\dagger Q_2 + E_0^2)]Q_2^\dagger\psi_0^3 = E_0^3 Q_2^\dagger\psi_0^3 \tag{II.39}$$

We then conclude that $Q_2^\dagger$ satisfies the intertwining relationship

$$Q_3^\dagger H_3 = H_2 Q_2^\dagger \tag{II.40}$$

It follows that

$$Q_2^\dagger\psi_0^3 = \sqrt{E_1^2 - E_0^2}\,\psi_1^2 \tag{II.41}$$

and using eq II.37,

$$Q_2 Q_2^\dagger\psi_0^3 = (E_1^2 - E_0^2)\psi_0^3 = E_0^3\psi_0^3 \tag{II.42}$$

Thus, we conclude that

$$E_0^3 = E_1^2 - E_0^2 \tag{II.43}$$

This procedure can be continued by defining the third superpotential, W_3, as

$$W_3 = -\frac{\mathrm{d}}{\mathrm{d}x}\ln\psi_0^3 \tag{II.44}$$

The charge operators are

$$Q_3 = \frac{\mathrm{d}}{\mathrm{d}x} + W_3 \tag{II.45}$$

and

$$Q_3^\dagger = -\frac{\mathrm{d}}{\mathrm{d}x} + W_3 \tag{II.46}$$

It is then easy to express H_3 in terms of the third sector charge operators:

$$H_3 = Q_3^\dagger Q_3 + E_0^3 \tag{II.47}$$

The first excited state equation for the third sector is then

$$H_3\psi_1^3 = E_1^3\psi_1^3 \tag{II.48}$$

so that

$$Q_3 Q_3^\dagger\psi_1^3 = (E_1^3 - E_0^3)\psi_1^3 \tag{II.49}$$

We then apply Q_3 to the above equation to find

$$(Q_3 Q_3^\dagger)Q_3\psi_1^3 = E_1^3 Q_3\psi_1^3 \tag{II.50}$$

Then, the fourth sector Hamiltonian is defined as

$$H_4 = Q_3 Q_3^\dagger + E_0^3 \tag{II.51}$$

and the ground state equation for sector four is

$$H_4\psi_0^4 = E_0^4\psi_0^4 = (E_1^3 - E_0^3)\psi_0^4 \tag{II.52}$$

One deduces also the next intertwining relation

$$Q_3 H_3 = H_4 Q_3 \tag{II.53}$$

with the isospectral relation being

$$E_0^4 = E_1^3 - E_0^3 \tag{II.54}$$

Clearly, the different sector wave functions result from the application of the charge operators:

$$Q_3\psi_1^3 = \sqrt{E_1^3 - E_0^3}\,\psi_0^4 \tag{II.55}$$

$$Q_3^\dagger\psi_0^4 = \sqrt{E_0^4}\,\psi_1^3 \tag{II.56}$$

It is clear that this procedure can be continued until one exhausts the number of bound excited states supported by H_1. We also see that determining the excited state energies and wave functions for H_1 involves solving for the ground state energies and wave functions for each sector Hamiltonian, H_j, $j > 1$.

III. SUSY-QM Family of Anharmonic Oscillators

The type of system we use to give a proof of principle in this paper is the anharmonic oscillator that is ubiquitous in chemistry. For example, all nuclear vibrations in molecules are anharmonic, with the effect increasing as the vibrational energy gets closer to the dissociation limit.[3] Anharmonicity also results from the effects of rotation, through the centrifugal potential. For the one-dimensional case, we consider an oscillator on the domain $-\infty < x < \infty$. In order to have potentials that are guaranteed to possess bound states, we shall postulate a superpotential

$$W(x) = \sum_{j=0}^{J} d_j x^{2j+1} \tag{III.1}$$

Then, the corresponding sector 1 potential, $V_1(x)$, is

$$V_1(x) = \sum_{j=0}^{J}\sum_{j'=0}^{J} d_j d_{j'} x^{2(j+j'+1)} - \sum_{j=0}^{J} d_j(2j+1)x^{2j} \tag{III.2}$$

The "charge" operators are given by

$$Q_1 = \frac{\mathrm{d}}{\mathrm{d}x} + W_1 \tag{III.3}$$

and

$$Q_1^{\dagger} = -\frac{\mathrm{d}}{\mathrm{d}x} + W_1 \tag{III.4}$$

Then, the first sector ground state for a general member of this family is

$$\psi_0^{+}(x) = N\exp\left[-\sum_{j=0}^{J} \frac{d_j x^{2j+2}}{(2j+2)}\right] \tag{III.5}$$

We stress that contrary to the periodic case, the solution of the sector two equation,

$$Q^{\dagger}\psi_0^2(x) = 0 \tag{III.6}$$

is not allowed because it is not normalizable. Thus, the ground state for the second sector satisfies

$$Q_1Q_1^{\dagger}\psi_0^2(x) = E_0^2\psi_0^2(x) = E_1^1\psi_0^2(x) \tag{III.7}$$

where

$$E_1^1 \neq 0 \tag{III.8}$$

However, once $\psi_0^2(x)$ is known, one can generate the first excited state $\psi_1^1(x)$ according to

$$Q_1^{\dagger}\psi_0^2(x) = \sqrt{E_0^2}\psi_0^1(x) \tag{III.9}$$

The energy, E_1^1, of $\psi_1^1(x)$ is, of course, equal to E_0^2.

We remark that the ground state, $\psi_0^1(x)$ is equal to the product of the ground states for each separate term in W. Thus,

$$\psi_0^1(x) = N\prod_{j=0}^{J} \mathrm{e}^{d_j x^{2j+2}/(2j+2)} \tag{III.10}$$

where N is the normalization constant. This is true even though $V_1(x)$ contains cross terms of the form

$$d_j d_{j'} x^{2(j+j'+1)},\ j \neq j' \tag{III.11}$$

In fact, even more general anharmonic oscillators can be dealt with. Thus, any function, $g(x)$ can be added to $W(x)$ in eq III.1, provided only that $\mathrm{e}^{-\int_0^x g(x')\mathrm{d}x'}$ is L^2. Thus, not only polynomic anharmonic potentials can be treated but many others. Of course, the resulting potential will involve added terms such as $g^2(x)$, along with cross products of $g(x)$ with $W(x)$ of eq III.1, and also $(\mathrm{d}g)/(\mathrm{d}x)$.

IV. Two Example Anharmonic Oscillator Systems

We now consider two specific examples of anharmonic oscillators. In the following section we will explore the computational aspects of the anharmonic oscillator, using these systems. To illustrate this approach to polynomic anharmonic oscillation we define $W(x)$ to be

$$W_1(x) = x^3 + 2x \tag{IV.1}$$

which obviously yields a potential for the first sector of

$$V_1(x) = x^6 + 4x^4 + x^2 - 2 \tag{IV.2}$$

It should be noted that x is defined on the domain $-\infty < x < \infty$.

We can thus define H_1 as:

$$H_1 = \left[-\frac{\mathrm{d}}{\mathrm{d}x} + W_1(x)\right]\left[\frac{\mathrm{d}}{\mathrm{d}x} + W_1(x)\right] \tag{IV.3}$$

which satisfies the equation

$$H_1\psi(x)_0^{(1)} = 0 \tag{IV.4}$$

and possesses an analytic ground state wave function of

$$\psi_0^{(1)} = N\mathrm{e}^{-(x^4/4+x^2)} \tag{IV.5}$$

To get the second Hamiltonian in the hierarchy we next define H_2 as

$$H_2 = \left[\frac{\mathrm{d}}{\mathrm{d}x} + W_1(x)\right]\left[-\frac{\mathrm{d}}{\mathrm{d}x} + W_1(x)\right] \tag{IV.6}$$

so

$$V_2 = x^6 + 4x^4 + 7x^2 + 2 \tag{IV.7}$$

and we must solve the equation

$$H_2\psi_0^{(2)} = E_0^{(2)}\psi_0^{(2)} \tag{IV.8}$$

Possessing $\psi_0^{(2)}$, we may develop the next Hamiltonian in the hierarchy. To do so, we begin by expressing H_2 in the following form

$$H_2 = \left[-\frac{\mathrm{d}}{\mathrm{d}x} + W_2(x)\right]\left[\frac{\mathrm{d}}{\mathrm{d}x} + W_2(x)\right] + E_0^{(2)} \tag{IV.9}$$

where

$$W_2(x) = -\frac{\mathrm{d}}{\mathrm{d}x}\ln \psi_0^{(2)} \tag{IV.10}$$

It should be obvious that

$$Q_2H_2\psi_1^{(2)} = E_1^{(2)}Q_2\psi_1^{(2)} \tag{IV.11}$$

leading to

$$Q_2Q_2^{\dagger}Q_2\psi_1^{(2)} = (E_1^{(2)} - E_0^{(2)})Q_2\psi_1^{(2)} \tag{IV.12}$$

with

$$\psi_0^{(3)} = \frac{Q_2\psi_1^{(2)}}{\sqrt{E_1^{(2)} - E_0^{(2)}}} \tag{IV.13}$$

It should be noted that from this point, one can obviously generate as many Hamiltonians as needed. It should also be noted that the excited state wave functions can be obtained by using the charge operators we have previously defined.

The second example results from taking

$$W_1(x) = x^3 + x + \mathrm{e}^x \tag{IV.14}$$

In this case,

$$V_1(x) = x^6 + 2x^4 + 2x^3\mathrm{e}^x + 2x\,\mathrm{e}^x + x^2 + e^{2x} - 3x^2 - \mathrm{e}^x - 1 \tag{IV.15}$$

Then,

$$H_1 = \left[-\frac{\mathrm{d}}{\mathrm{d}x} + x^3 + x + \mathrm{e}^x\right]\left[\frac{\mathrm{d}}{\mathrm{d}x} + x^3 + x + \mathrm{e}^x\right] \tag{IV.16}$$

with

$$H_1\psi_0^1 = 0 \tag{IV.17}$$

and the analytical ground state is

$$\psi_0^{(1)} = N\mathrm{e}^{-(x^4/4+x^2+\mathrm{e}^x)} \tag{IV.18}$$

Then the second sector Hamiltonian is

$$H_1 = \left[\frac{\mathrm{d}}{\mathrm{d}x} + x^3 + x + \mathrm{e}^x\right]\left[-\frac{\mathrm{d}}{\mathrm{d}x} + x^3 + x + \mathrm{e}^x\right] \tag{IV.19}$$

The ground state satisfies

$$H_2\psi_0^2 = E_0^2\psi_0^2 \tag{IV.20}$$

which must be solved numerically. However, having ψ_0^2, one then obtains

$$W_2(x) = -\frac{\mathrm{d}}{\mathrm{d}x}\ln\,\psi_0^{(2)} \tag{IV.21}$$

and

$$H_3 = \left[\frac{\mathrm{d}}{\mathrm{d}x} + W_2(x)\right]\left[-\frac{\mathrm{d}}{\mathrm{d}x} + W_2(x)\right] \tag{IV.22}$$

This procedure is continued until the bound excited states of H_1 are exhausted.

TABLE 1: Energies for the Anharmonic Polynomic Oscillator Using Hierarchy of Hamiltonians

n	${}_N\psi_0^n$	H_1	${}_N\psi_1^n$	H_2
0	${}_{44}\psi_0^1$	$6.944\,1187 \times 10^{-7}$	${}_{34}\psi_0^1$	5.024450
1	${}_{52}\psi_1^1$	5.024 449	${}_{42}\psi_0^1$	11.696825
2	${}_{62}\psi_2^1$	11.696 820	${}_{50}\psi_0^1$	19.497666

TABLE 2: Wave Function Errors for the Anharmonic Polynomic Oscillator Using the Standard Variational Method for Each Hierarchy Hamiltonian

n	${}_N\psi_0^n$	L_2	L_∞
0	${}_{56}\psi_0^1$	$5.835\,283 \times 10^{-7}$	$1.110\,223 \times 10^{-16}$
1	${}_{78}\psi_1^1$	$1.975\,656 \times 10^{-7}$	$4.019\,723 \times 10^{-16}$
0	${}_{68}\psi_0^2$	$2.303\,928 \times 10^{-7}$	$2.220\,446 \times 10^{-16}$

V. Computational Considerations for the Anharmonic Oscillator

We now turn to the proof of principle for this approach as a computational scheme to obtain improved excited state energies and wave functions in the Rayleigh–Ritz variational method. We should note that these results can be generalized to any system where a hierarchy of Hamiltonians can be generated because of the nature of the Rayleigh–Ritz scheme. In the standard approach one calculates the energies and wave functions variationally, relying on the Hylleraas–Undheim theorem for convergence.[2] This, however, is unattractive for higher energy states because they require a much larger basis to converge to the same error. **We stress that this is true regardless of the specific basis set used.** Of course, some bases will be more efficient than others but it is generally true that for a given basis, the Rayleigh–Ritz result is less accurate for excited states. We address this situation by always solving for ground states in the variational part of the problem.

To demonstrate our computational scheme, we investigate the first example system from the previous section. For this potential (eq IV.2), exact solutions are known for all states of H_1. We use the exact results to assess the accuracy of the variational calculations. For our first variational calculations, we use the harmonic oscillator basis functions where:

$$\phi_n(x) = \frac{1}{\sqrt{2^n n!\sqrt{\pi}}}H_n(x)\mathrm{e}^{-x^2/2} \tag{V.1}$$

with each matrix element determined using

$$\int_{-\infty}^{\infty} \phi_{n'}(x)x^j\phi_n(x)\mathrm{d}x \tag{V.2}$$

Using the hierarchy of Hamiltonians, we present the converged eigenvalues in Table 1. In Table 1, all energies were obtained for each of the Hamiltonians, H_1 and H_2, by standard variational calculations using basis set sizes to achieve an accuracy of 10^{-6}. It is easily seen that the ground state of H_2 is degenerate with the first excited state of H_1. This results from the intertwining relations. The energies are accurate to six significant figures. More interesting is the behavior of the excited state wave functions. Using the Cauchy criterion to measure convergence, we show the basis set size (N) needed in a standard variational approach to obtain various eigenstates to the accuracy shown in Table 2. Clearly, excited state wave functions require substantially larger basis sets to achieve a high degree of accuracy. In Table 3 we show the results obtained for the same

TABLE 3: Wave Function Errors for the Anharmonic Polynomic Oscillator Using Charge Operators to Find Excited States

n	ΔN	${}_N\psi_0^n$	L_2	L_∞
1	4	${}_{74}\psi_1^1$	$4.083\,823 \times 10^{-7}$	$2.086\,041 \times 10^{-16}$

TABLE 4: Energies for the Anharmonic Non-Polynomic Oscillator Using Hierarchy of Hamiltonians, Determined Variationally

n	${}_N\psi_0^n$	H_1	${}_N\psi_1^n$	H_2
0	${}_{50}\psi_0^1$	$2.703\,955 \times 10^{-6}$	${}_{44}\psi_0^1$	5.263075
1	${}_{60}\psi_1^1$	5.263 075	${}_{56}\psi_0^1$	12.109712
2	${}_{64}\psi_2^1$	12.109 717	${}_{66}\psi_0^1$	20.186019

TABLE 5: Errors for the Anharmonic Non-Polynomic Oscillator Wave Functions Using Hierarchy of Hamiltonians All Determined Variationally

n	${}_N\psi_0^n$	L_2	L_∞
0	${}_{70}\psi_0^1$	$3.715\,8761 \times 10^{-7}$	$2.220\,446 \times 10^{-16}$
1	${}_{88}\psi_1^1$	$6.477\,328 \times 10^{-8}$	$1.221\,245 \times 10^{-15}$
0	${}_{76}\psi_0^2$	$5.659\,010 \times 10^{-7}$	$2.109\,424 \times 10^{-15}$

TABLE 6: Errors for the Anharmonic Non-Polynomic Oscillator Using Wave Functions Charge Operators to Find Excited States by Applying the Correct Charge Operator to the Appropriate Ground State

n	ΔN	${}_N\psi_0^n$	L_2	L_∞
1	14	${}_{74}\psi_1^1$	$9.750\,546 \times 10^{-7}$	$3.181\,791 \times 10^{-16}$

excited state wave functions obtained by applying the charge operator to the ground state wave function for H_2. Again, N denotes the basis set required, and ΔN is the reduction of basis set achieved by use of the charge operators.

To find the solutions we used both LAPACK routines to find these eigenvalues and vectors and GSL routines for numerical integration. Clearly, the use of the hierarchy of Hamiltonians and the use of charge operators provides more rapid convergence. which provides us with better methods to calculate the excited states.

We performed the same calculations and found similar results for the second system described by $W = x^3 + x + e^x$. Because the excited states of this oscillator are not known analytically, we use the Cauchy convergence criterion

$$\int_{-\infty}^{\infty} |{}_N\psi_n - {}_{N-1}\psi_n|^2 dx \qquad (V.3)$$

where N is the basis size. This system is nontrivial since we are not aware of any analytic solutions. In Table 4, we give the converged energy levels (to 5 significant figures) obtained by standard variational calculations applied to H_1 and H_2. In Table 5, we show the basis set sizes needed in standard variational calculations to converge the wave functions for H_1 and H_2 (again, the Cauchy criterion of convergence was used.) Finally, in Table 6, we show the results for excited states obtained using the charge operators applied to the ground state wave functions of H_2. Again, ΔN shows the reduction in the basis size gained by the charge operator approach.

Finally, we compared the numerical accuracy of the first excitation energy of the anharmonic oscillator described by eq IV.2, but now using a n -point discrete variable representation (DVR)[16] based upon the Tchebychev polynomials to compute the eigenspectra of the first and second sectors. In Figure 1 we show the numerical error in the first excitation energy by comparing $E_1^1(n)$ (the first excited state energy from the standard variational calculation with n-DVR basis functions) and $E_0^2(n)$ (the ground state of the sector 2 Hamiltonian computed with n-DVR basis functions) from an n point DVR to the numerically "exact" value corresponding to a 100 point DVR,

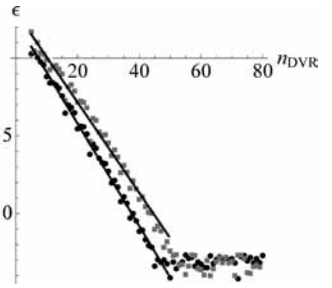

Figure 1. Convergence of first excitation energy E_1^1 for model potential $V_1 = x^6 + 4x^4 + x^2 - 2$ using a n -point discrete variable representation (DVR). Gray squares: $\varepsilon = \log_{10}|E_1^1(n) - E_1^1(\text{exact})|$, Black squares: $\varepsilon = \log_{10}|E_0^2(n) - E_1^1(\text{exact})|$. Dashed lines are linear fits.

$$\varepsilon_1^1(n) = \log_{10}|E_1^1(n) - E_1^1(\text{exact})|$$

Likewise,

$$\varepsilon_0^2(n) = \log_{10}|E_0^2(n) - E_1^1(\text{exact})|$$

For any given basis size, $\varepsilon_0^2 < \varepsilon_1^1$. Moreover, over a range of $15 < n < 40$ points, the excitation energy computed using the second sector's ground state is between 10 and 100 times more accurate than $E_1^1(n)$. This effectively reiterates our point that by using the SUSY hierarchy, one can systematically improve upon the accuracy of a given variational calculation. It also shows that our conclusion does not depend on the basis set used.

VI. Conclusions

Although anharmonic oscillator models are useful for a wide variety of problems in both chemistry and physics, it should be clear that other systems should show similar behavior. The SUSY-QM approach enabled us to develop a hierarchy of isospectral Hamiltonians. This also led to the introduction of charge operators that transform wave functions between the various sectors, and the energies are always determined in a ground state setting. Because these are most easily and accurately obtained by the variational method, we realize a significant reduction in the basis size needed to yield accurate excited state wave functions. We then considered two specific examples of anharmonic oscillators. We concluded that using the SUSY hierarchy of Hamiltonians and charge operators, provided faster convergence to the same level of accuracy and thus, provides a better method than the standard variational approach. In some cases, only half as many basis functions were needed to generate the ground state wave function as were required for the first excited state of the same sector. As a result, the computational time for molecular models using anharmonic potentials will be significantly reduced, without sacrificing accuracy.

We also stress that our results do not depend on precisely what basis set is used for the calculations. Rather we are capitalizing on the general behavior of the Rayleigh−Ritz variational method with regard to accuracy and convergence rate for ground versus excited states of a given Hamiltonian.

Finally, we comment that we have recently generalized the SUSY formalism to any number of dimensions.[17]

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