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Demonstration of the Gunnarsson-Lundqvist Theorem and the Multiplicity of Potentials for Excited States

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Abstract

The Gunnarsson-Lundqvist (GL) theorem of density functional theory states that there is a one-to-one relationship between the density of the lowest nondegenerate excited state of a given symmetry and the external potential. As a consequence, knowledge of this excited state density determines the external potential *uniquely*. (The GL theorem is the equivalent for such excited states of the Hohenberg-Kohn (HK) theorem for nondegenerate ground states.) For other excited states, there is no equivalent of the GL or HK theorem. For these states, there thus exist multiple potentials that generate the excited state density. We show, by example, the satisfaction of the GL theorem, and the multiplicity of potentials for excited states.

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I. INTRODUCTION

Matter – atoms, molecules, solids – can be described as a system of N electrons in the presence of an external electrostatic field $\boldsymbol{\mathcal{F}}^{\mathrm{ext}}(\mathbf{r}) = -\nabla v(\mathbf{r})$, where $v(\mathbf{r})$ is a scalar potential. For such a system in a nondegenerate ground state, the Hohenberg-Kohn (HK) theorem [1] proves via the variational principle for the energy that there is a one-to-one relationship between the external potential $v(\mathbf{r})$ and the ground state density $\rho(\mathbf{r})$. Hence, knowledge of the density $\rho(\mathbf{r})$ *uniquely* determines the external potential $v(\mathbf{r})$ to within an additive constant. The significance of this is that the knowledge of the ground state density $\rho(\mathbf{r})$ of a physical system then *uniquely* determines the Hamiltonian $\hat{H}$ since the kinetic and electron-interaction operators are assumed known, and via the solution of the Schrödinger equation, all the properties of that system.

(As a consequence of the HK theorem, the ground state wave function Ψ is a functional of the density $\rho(\mathbf{r})$. Via a density preserving unitary transformation, it has been shown [2, 3] that the wave function must also be a functional of a gauge function $\alpha(\mathbf{R}); \mathbf{R} = \mathbf{r}_1, \ldots, \mathbf{r}_N$ in order to ensure that the wave function written as a functional is gauge variant. Thus, $\Psi = \Psi[\rho, \alpha]$. The HK theorem is valid for each choice of gauge function $\alpha(\mathbf{R})$ [2, 3]. It follows from the HK theorem that all physical observables are unique functionals of the ground state density$\rho(\mathbf{r})$.)

Within conventional Schrödinger wave function theory, the variational principle is also applicable to the lowest excited state of a given symmetry. In the variational procedure, one restricts the approximate wave functions to have the given excited state symmetry, and the lowest state of that symmetry is achieved by energy minimization. A corresponding HK theorem for such states can therefore be proved. The proof is for v-representable densities derived from wave functions that have the given excited state symmetry. Thus, knowledge of the density $\rho^e(\mathbf{r})$ for such an *excited* state then *also* determines the external potential $v(\mathbf{r})$ *uniquely* to within a constant, and thereby the Hamiltonian $\hat{H}$. We refer to this as the Gunnarsson-Lundqvist (GL) theorem [4] as these authors originally proved the above theorem for the special case of spin-density functional theory. (The excited state wave function Ψ^e is a functional *solely* of the density $\rho^e(\mathbf{r})$, and of course of a gauge function $\alpha(\mathbf{R})$ to ensure that Ψ^e written as a functional is gauge variant. Thus, for the lowest excited state of a given symmetry $\Psi^e = \Psi^e[\rho^e, \alpha]$. The GL theorem is valid for each choice of gauge function $\alpha(\mathbf{R})$. In addition, all properties are also unique functionals of the density $\rho^e(\mathbf{r})$.)

For the other excited states, it is known [4–6] that there is no equivalent of the HK theorem. In other words, there is no one-to-one relationship between the excited state density $\rho^e(\mathbf{r})$ and the external potential $v(\mathbf{r})$. As knowledge of the density $\rho^e(\mathbf{r})$ of these excited states does not uniquely determine the external potential $v(\mathbf{r})$, the implication is that there could exist several potentials $v(\mathbf{r})$ for which the corresponding Schrödinger equations all generate the same excited state density $\rho^e(\mathbf{r})$.

In this paper we demonstrate the satisfaction of the GL theorem, and the multiplicity of the potentials for excited states for a model system of two noninteracting fermions in a one-dimensional infinite potential well. (This model is the original system.) In addition to demonstrating the lack of an HK theorem for excited states, the results of our calculations are interesting in their own right as discussed below. In particular we demonstrate the following: (a) For the first excited triplet state – the lowest excited state of this symmetry – we show that the potential that generates the corresponding excited state density is *unique*; (b) For the second excited triplet state, we show (i) that there exists *no other* potential that generates the excited state density for this state with an orbital configuration which is the *same* as the original; (ii) that there exist multiple potentials which generate this excited state density, but with orbital configurations and eigenvalues that *differ* from each other and from the original; and (iii) that there exist multiple potentials with the *same* orbital configuration, but with *different* eigenvalues, that generate the excited state density. These calculations for the multiple potentials, orbitals, and eigenvalues are *exact*. We note that although the solutions of the original potential are analytically obtainable, the determination of the multiple alternate potentials is difficult particularly in the region close to and at the boundaries. We have overcome this problem by relating the orbitals of the original potential to those of the other (multiple) potentials via a rotation. As such we provide the structure of the multiple potentials and corresponding orbitals including the region close to and at the boundaries. We also provide the resulting self-consistently determined eigenvalues.

For completeness we note that in order to demonstrate the lack of a HK theorem for excited states, the above model problem for the second excited triplet state has been studied by Gaudoin and Burke [7] within the linear response approximation. Their search is restricted to those potentials with this *fixed* excited state configuration for the model fermions. They show that there are multiple potentials for this configuration, and that this multiplicity is related to the positive eigenvalues of the nonlocal susceptibility for excited states. The results of these authors, therefore, differ from ours. Additionally, they do not provide the structure of the multiple potentials near and at the boundaries. Following the description of our methodology and the subsequent description of our exactly determined structures, we make comparisons with the results of these authors. Finally, employing the Zhao-Parr numerical method [8], which determines local potentials that reproduce a known density, Samal et al [9] state that they have replicated the results of Gaudoin-Burke.

In Sec. II we describe the model system of noninteracting fermions in an arbitrary local effective potential, and derive the general equation required for the determination of the multiple potentials. In Sec. III we demonstrate the satisfaction of the GL theorem for the first excited triplet state for the case of an infinite potential well. For the second excited triplet state of this potential we determine in Sec. IV multiple potentials that generate the excited state density thereby demonstrating the lack of HK theorem for this state. We conclude in Sec. V by summarizing the broader understanding of the issue of uniqueness/nonuniqueness of the potentials that generate a ground or excited state density.

II. MODEL SYSTEM

Consider a system of 2 noninteracting fermions in a local one-dimensional potential $v(x)$. The Schrödinger equation for these fermions in atomic units ($e = \hbar = m = 1$) is

$$\left[-\frac{1}{2}\frac{d^2}{dx^2} + v(x)\right]\phi_i(x) = \epsilon_i \phi_i(x), \quad i = 1, 2. \tag{1}$$

Suppose there exists another local potential $v'(x)$ which generates the same density as that of $v(x)$. The corresponding Schrödinger equation is

$$\left[-\frac{1}{2}\frac{d^2}{dx^2} + v'(x)\right]\phi'_i(x) = \epsilon'_i \phi'_i(x), \quad i = 1, 2. \tag{2}$$

The density $\rho(x)$ corresponding to the two potentials is

$$\rho(x) = \phi_1^2(x) + \phi_2^2(x) = \phi_1'^2(x) + \phi_2'^2(x). \tag{3}$$

Suppose one may obtain $\phi'_i(x)$ from $\phi_i(x)$ via a rotation $\theta(x)$, and that such a rotation exists:

$$\begin{aligned}\begin{pmatrix}\phi'_1(x)\\ \phi'_2(x)\end{pmatrix} &= \begin{pmatrix}\cos\theta(x) & \sin\theta(x)\\ -\sin\theta(x) & \cos\theta(x)\end{pmatrix}\begin{pmatrix}\phi_1(x)\\ \phi_2(x)\end{pmatrix}\\ &= \begin{pmatrix}\phi_1(x)\cos\theta(x)+\phi_2(x)\sin\theta(x)\\ -\phi_1(x)\sin\theta(x)+\phi_2(x)\cos\theta(x)\end{pmatrix}.\end{aligned} \tag{4}$$

From Eq. (2) it follows that

$$v'(x) = \epsilon'_1 + \frac{1}{2\phi'_1(x)}\ddot{\phi}'_1(x) = \epsilon'_2 + \frac{1}{2\phi'_2(x)}\ddot{\phi}'_2(x), \tag{5}$$

with $\ddot{\phi}'_i(x) = d^2\phi'_i(x)/dx^2$. The corresponding equation for $v(x)$ follows from Eq. (1). From these equations one obtains

$$\Delta = \epsilon_2 - \epsilon_1 = \frac{1}{2\phi_1(x)\phi_2(x)}\frac{d}{dx}\big(\phi_2(x)\dot{\phi}_1(x) - \phi_1(x)\dot{\phi}_2(x)\big) \tag{6}$$

and

$$\Delta' = \epsilon'_2 - \epsilon'_1 = \frac{1}{2\phi'_1(x)\phi'_2(x)}\frac{d}{dx}\big(\phi'_2(x)\dot{\phi}'_1(x) - \phi'_1(x)\dot{\phi}'_2(x)\big), \tag{7}$$

where $\dot{\phi}_i(x) = d\phi_i(x)/dx$ etc. On substituting for $\phi'_1(x), \phi'_2(x)$ from Eq. (4) in Eq. (7) one then obtains

$$\begin{aligned}&\frac{d}{dx}\Big[\dot{\theta}(x)\big\{\phi_1^2(x)+\phi_2^2(x)\big\} + \big\{\phi_2(x)\dot{\phi}_1(x) - \phi_1(x)\dot{\phi}_2(x)\big\}\Big]\\ &= \Delta'\Big[2\phi_1(x)\phi_2(x)\cos 2\theta(x) + \big\{\phi_2^2(x) - \phi_1^2(x)\big\}\sin 2\theta(x)\Big],\end{aligned} \tag{8}$$

or equivalently on employing Eq. (3) and Eq. (6) in Eq. (8)

$$\rho(x)\ddot{\theta}(x) + \dot{\rho}(x)\dot{\theta}(x) + f(\phi_1, \phi_2, \Delta, \Delta', \theta) = 0, \tag{9}$$

where

$$f = 2\Delta\phi_1(x)\phi_2(x) - \Delta'\Big[2\phi_1(x)\phi_2(x)\cos 2\theta(x) + \{\phi_2^2(x) - \phi_1^2(x)\}\sin 2\theta(x)\Big]. \tag{10}$$

This is the general differential equation for the rotation $\theta(x)$ for the determination of the alternate system. Thus, for a given $\phi_1(x), \phi_2(x), \Delta$, and $\rho(x)$, one solves Eq. (9) for the rotation $\theta(x)$ and Δ'. This leads to the orbitals $\phi'_1(x)$ and $\phi'_2(x)$ via Eq. (4), and the potential $v'(x)$ via Eq. (5). It is evident that when $\theta(x) = 0$ with $\theta \in [0, 2\pi]$, then $f = 2(\Delta - \Delta')\phi_1(x)\phi_2(x) = 0$, or that $\Delta' = \Delta$, $\phi'_1(x) = \phi_1(x)$ and $\phi'_2(x) = \phi_2(x)$. Thus,

$v'(x) = v(x)$ and there is no new solution. The orbitals $\phi'_1(x)$ and $\phi'_2(x)$ must be normalized. Thus, solutions of Eq. (9) must be such as to ensure normalization of $\phi'_1(x)$. Then $\phi'_2(x)$ is automatically normalized via Eq. (3). (Note that for $\theta(x) =$ constant, the primed orbitals are simply linear combinations of the unprimed orbitals (see Eq. (4)). As such no new physics is garnered for such a case.)

The potential $v(x)$ that we consider is the infinite potential well:

$$v(x) = \begin{array}{ll} \infty & \text{for } x = 0, 1 \\ 0 & \text{for } 0 < x < 1. \end{array} \tag{11}$$

The orbitals $\phi_n(x)$ and eigenvalues E_n for the nth state are

$$\phi_n = \sqrt{2} \sin n\pi x \quad ; \quad E_n = \frac{n^2\pi^2}{2}. \tag{12}$$

The ground state of this system corresponds to the two fermions of opposite spin in the lowest state $n = 1$. The first (lowest) excited triplet state corresponds to one fermion in the lowest $n = 1$ state, and the second fermion with parallel spin in the $n = 2$ state. The configuration of the orbitals is 1-2, there being one node for the orbital in the $n = 2$ state. The second excited triplet state corresponds to one fermion in the $n = 1$ state and the second fermion of parallel spin in the $n = 3$ state with a 1-3 configuration and two nodes for the orbital in the excited state.

III. SATISFACTION OF THE GUNNARSSON-LUNDQVIST THEOREM

Employing the framework described in the previous section, we next demonstrate that for the first excited triplet state the potential $v(x)$ is *unique*, viz. that of Eq. (11). Thereby, the GL theorem is satisfied. For this state $\epsilon_1 = \pi^2/2$, $\epsilon_2 = 2\pi^2$, $\Delta = \epsilon_2 - \epsilon_1 = 3\pi^2/2$, the density

$$\rho(x) = 2[\sin^2(\pi x) + \sin^2(2\pi x)], \tag{13}$$

and the equation corresponding to Eq. (9) for the rotation $\theta(x)$ is

$$\begin{aligned} \rho(x)\ddot{\theta}(x) \; &+ \; \dot{\rho}(x)\dot{\theta}(x) + 6\pi^2 \sin(\pi x)\sin(2\pi x) \\ &- \; \Delta'[4\sin(\pi x)\sin(2\pi x)\cos 2\theta(x) + 2\{\sin^2(2\pi x) - \sin^2(\pi x)\}\sin 2\theta(x)] = 0. \end{aligned} \tag{14}$$

Note that since $\phi_1(x)$ is symmetric, $\phi_2(x)$ antisymmetric, and $\rho(x)$ symmetric about $x = 1/2$, then Eq. (14) dictates that $\theta(x)$ is antisymmetric so that $\theta(1/2) = 0$.

The structure of the solution in the limit as $x \to 0$ is

$$\theta(x) \underset{x\to 0}{\sim} \frac{a}{x} + b + cx + O(x^2). \tag{15}$$

To see that this is the general structure in the limit, consider the large $\theta(x)$ case for which the $\cos 2\theta(x)$ and $\sin 2\theta(x)$ oscillate rapidly and may be dropped from the equation. The Eq. (14) reduces to

$$\rho(x)\ddot{\theta}(x) + \dot{\rho}(x)\dot{\theta}(x) + 2\Delta\phi_1(x)\phi_2(x) = 0, \tag{16}$$

whose solution can be obtained analytically as

$$\theta(x) = C_2 + \frac{1}{25\pi}\Big[\tan^{-1}(2-\sqrt{5}\tan\frac{\pi x}{2})(25\pi - 4\sqrt{5}C_1)$$
$$+\tan^{-1}(2+\sqrt{5}\tan\frac{\pi x}{2})(25\pi + 4\sqrt{5}C_1) - 5C_1\cot\pi x\Big]. \tag{17}$$

The behavior of $\theta(x)$ of Eq. (16) in the limit $x \to 0$ is given by Eq. (15). As $\theta(x)$ is antisymmetric, the physical solution must be such that it is finite at the boundary. Thus, one needs to consider the limit $x \to 0$ of the different solutions of Eq. (14) possible. Furthermore, the physical solution then corresponds in Eq. (15) to the coefficient $a = 0$.

The procedure for determining the potential $v'(x)$ is the following. For a given value of Δ' and $\dot{\theta}(1/2)$, (the initial conditions), Eq. (14) is solved for $\theta(x)$. Then from Eq. (4), $\phi'_1(x)$ and $\phi'_2(x)$ are obtained. And $v'(x)$ obtained from Eq. (5). The orbitals $\phi'_1(x)$ and $\phi'_2(x)$ must also be normalized, i.e. satisfy the constraint

$$\int_0^1 \phi'_1(x)^2 dx - 1 = R = 0. \tag{18}$$

Note that not all $\theta(x)$ can satisfy Eq. (18). Once the normalized $\phi'_1(x)$ is determined, then $\phi'_2(x)$ is automatically normalized via Eq. (3).

In Fig. 1, we plot the function R of Eq. (18) as a function of $\dot{\theta}(1/2)$ for values of $\Delta' = 10, 30, 50$. The points $A_1, B_1, C_1; A_2, B_2, C_2$ etc., for which $R = 0$ correspond to $\phi'_1(x)$, (and therefore $\phi'_2(x)$), that are normalized. (The symmetrical points lead to the same solutions.) Next the limit $\theta(x)$ as $x \to 0$ is examined to determine the coefficient 'a' of Eq. (15). The values of 'a' as a function of Δ' are plotted in Fig. 2. Observe that of the normalized solutions corresponding to A_1, B_1, C_1, only the solution corresponding to A_1 is such that on examining the $\theta(x)$ as $x \to 0$ limit, the coefficient 'a' $= 0$. As indicated previously, this then corresponds to a physical solution. The coefficient 'a' $= 0$ at a value

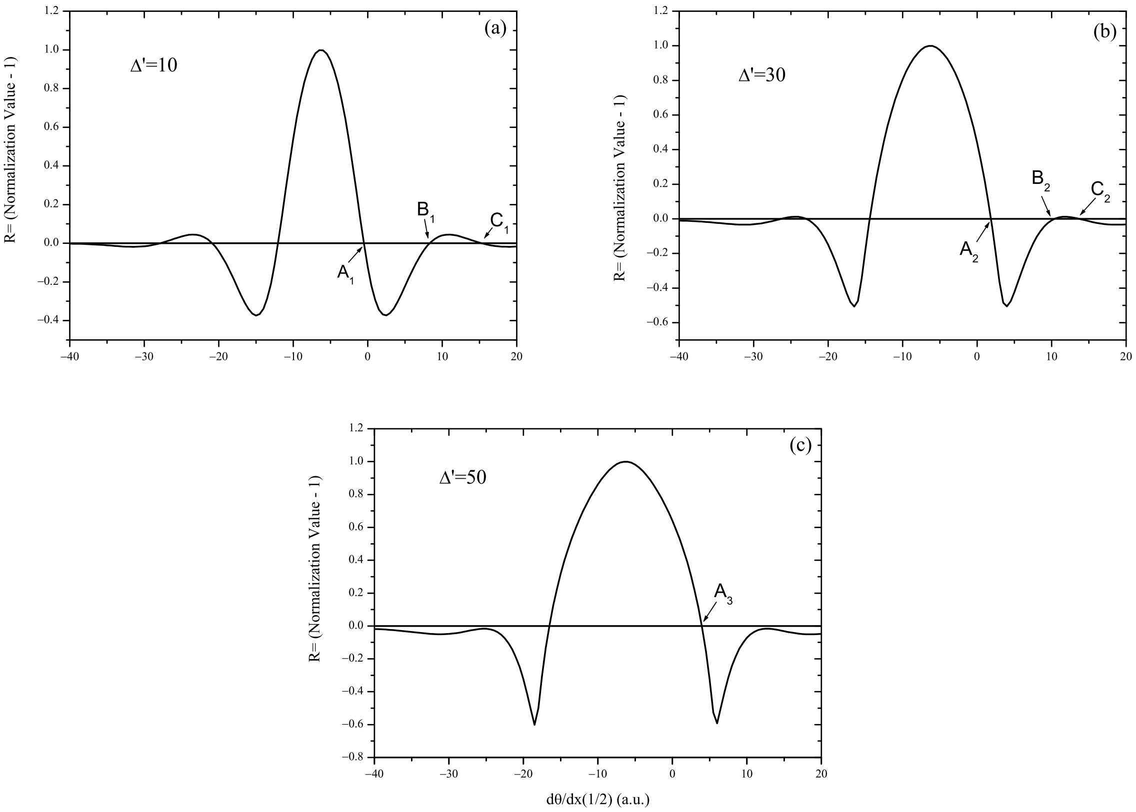

FIG. 1: The function R of Eq. (18) which is the normalization integral minus one versus the derivative of the rotation: $d\theta(x)/dx|_{x=1/2}$ for the first (lowest) excited triplet state. Panels a, b, c correspond to the difference in eigenvalues of the alternate system: $\Delta' = \epsilon'_2 - \epsilon'_1 = 10, 30, 50$ respectively.

of $\Delta' = 3\pi^2/2 \equiv \Delta$. Thus there exists only *one* solution which is the original one. Hence, for the density $\rho(x)$ of the lowest triplet state, there exists only one potential $v(x)$. This demonstrates the satisfaction of the GL theorem.

IV. MULTIPLICITY OF POTENTIALS FOR EXCITED STATES

We next demonstrate the lack of the HK theorem for excited states by determining multiple potentials $v'(x)$ that generate the density of the second excited triplet state of the two fermions in the potential $v(x)$ of Eq. (11). For this state $\epsilon_1 = \pi^2/2, \epsilon_2 = 9\pi^2/2, \Delta =$

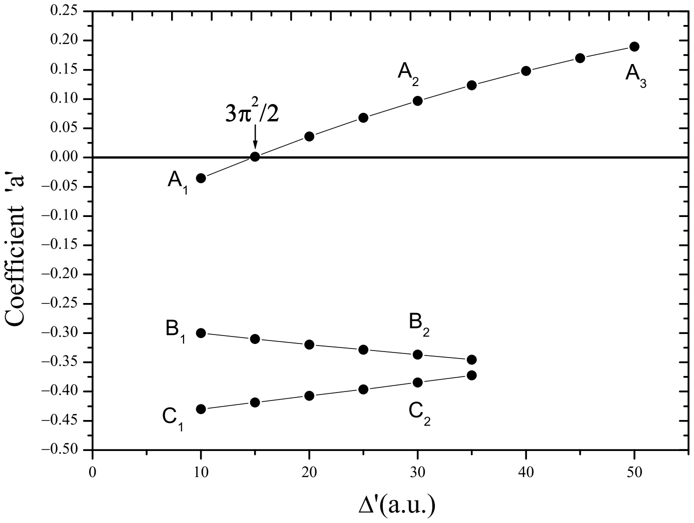

FIG. 2: The coefficient ‘a’ of Eq. (15) versus $\Delta' = \epsilon'_2 - \epsilon'_1$ the difference in eigenvalues of the alternate system for the first (lowest) excited triplet state.

$\epsilon_2 - \epsilon_1 = 4\pi^2 = 39.478$, and the density

$$\rho(x) = 2[\sin^2 \pi x + \sin^2 3\pi x]. \tag{19}$$

The equation corresponding to Eq. (9) for the rotation $\theta(x)$ is

$$\begin{aligned} &\rho(x)\ddot{\theta}(x) + \dot{\rho}(x)\dot{\theta}(x) + 16\pi^2 \sin(\pi x)\sin(3\pi x) \\ &= \Delta'\big[16\pi^2 \sin(\pi x)\sin(3\pi x)\cos 2\theta(x) + 2\{\sin^2(3\pi x) - \sin^2(\pi x)\}\sin 2\theta(x)\big] = 0. \end{aligned} \tag{20}$$

Eq. (20) requires that $\theta(x)$ is symmetric about $x = 1/2$ so that $\dot{\theta}(1/2) = 0$. With the initial conditions of Δ' and $\theta(1/2)$, Eq. (20) is solved for the rotation $\theta(x)$. The procedure for determining the orbitals $\phi'_1(x), \phi'_2(x)$ and the potential $v'(x)$ is the same as before. We emphasize that for all physical solutions, the rotation $\theta(x)$ is finite at the boundaries. The use of a rotation $\theta(x)$ to relate the original and new orbitals allows the determination of the structure of the new orbitals and potentials near and at the boundaries.

In Fig. 3, we plot the function R of Eq. (18) as a function of $\theta(1/2)$ for values of $\Delta' = 1, 20, 40$ and in Fig. 4 for $\Delta' = 60, 80, 160$. Note that values of $\theta(1/2)$ for which $R = 0$ correspond to the $\phi'_1(x)$ that are normalized.

We first note that there exist no alternate physical solutions $v'(x)$ for $\Delta' = \Delta = 4\pi^2 = 39.478$ with the 1-3 configuration of the original potential $v(x)$.

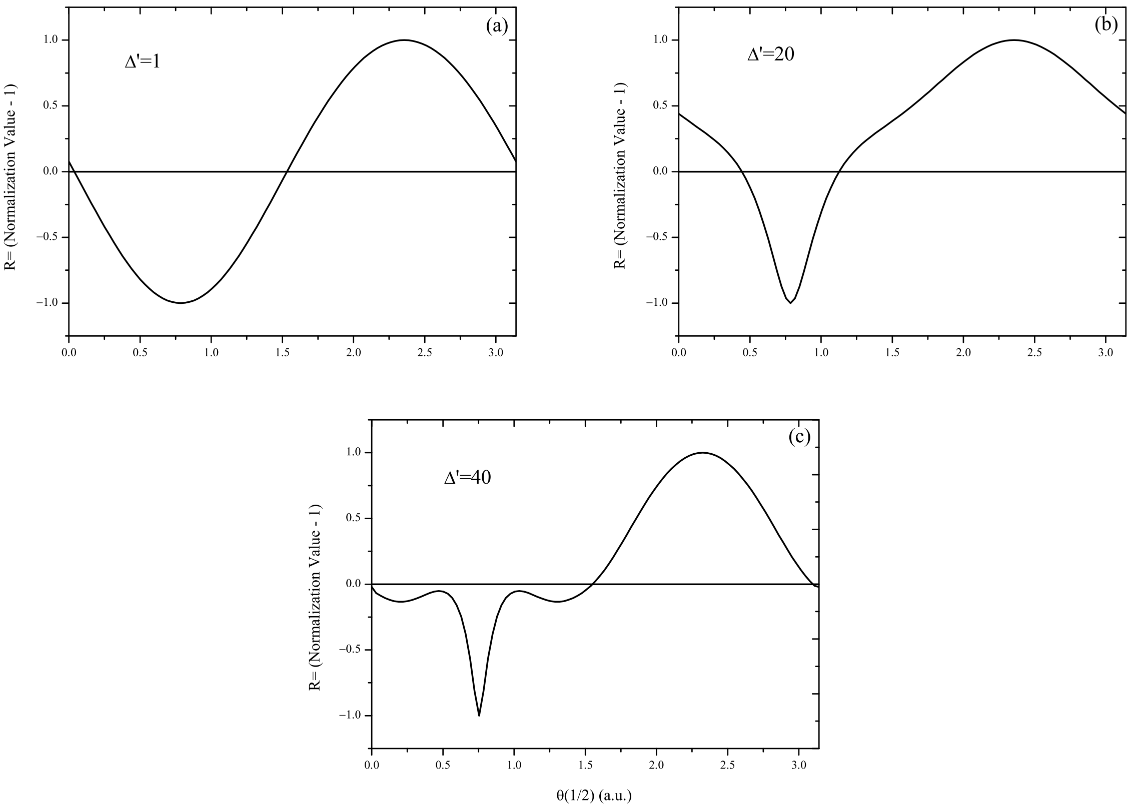

FIG. 3: The function R of Eq. (18) which is the normalization integral minus one versus the rotation $\theta(1/2)$ for the second excited triplet state. Panels a, b, c correspond to the eigenvalue difference $\Delta' = \epsilon'_2 - \epsilon'_1 = 1, 20, 40$ respectively.

In Fig. 5 we plot the functions (a) for the rotation $\theta(x)$, (b) the orbitals $\phi'_1(x), \phi'_2(x)$, and (c) the potential $v'(x)$ for $\Delta' = 160.077$. Observe, Fig. 5a, that $\theta(x)$ is symmetric about $x = 1/2$ and finite at the boundaries as expected for this state. Note from Fig. 5b, that this corresponds to a 3-5 configuration of the fermions: $\phi'_1(x)$ has 2 nodes, $\phi'_2(x)$ has 4 nodes. Finally, in Fig. 5c, note that the potential $v'(x)$ is symmetric about $x = 1/2$, and that its structure near and at the boundaries is explicitly given.

In Fig. 6 we plot $\theta(x), \phi'_1(x), \phi'_2(x), v'(x)$ for $\Delta' = 359.029$. Although the symmetry of these functions is the same as in Fig 5, the structure of these functions is different. Observe, however, Fig. 6b, that this case too corresponds to the fermions having a 3-5 configuration.

From Figs. 5 and 6 we see that there exist multiple potentials $v'(x)$ with the *same* 3-5 configuration but with different eigenvalues and eigenfunctions that generate the excited

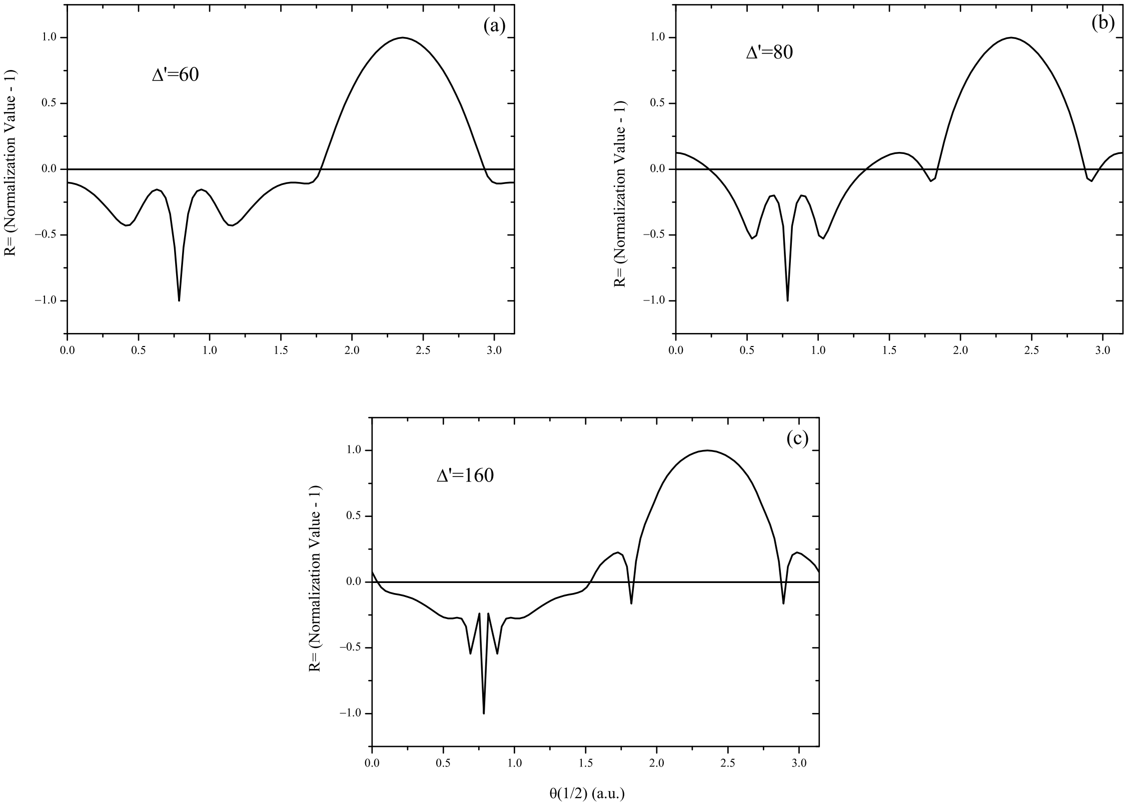

FIG. 4: The same as Fig. 3 but for $\Delta' = 60, 80, 160$.

state density.

Finally, in Fig. 7, we plot $\theta(x), \phi_1'(x), \phi_2'(x), v'(x)$ for $\Delta' = 600.85$. From Fig. 7b it is evident that this is a 3-7 configuration of the fermions: $\phi_1'(x)$ has 2 nodes; $\phi_2'(x)$ has 6 nodes. Thus, there exist yet another potential $v'(x)$ with the fermions having yet another different configuration and eigenvalues that generate the excited state density.

The fact of existence of such multiple potentials $v'(x)$ that generate the same excited state density shows that with the exception of the lowest excited state of a given symmetry, there is no HK theorem for excited states.

To conclude this section we compare our exactly determined results with those of Gaudoin-Burke [7] obtained via linear response theory. The work of these authors is for a *fixed* level of excitation or orbital configuration. Thus, for the second excited triplet state, they show a second potential $[v'(x)]$ that reproduces the excited state density but with the same 1-3 orbital configuration. (See Fig. 1 of [7].) The potential is *asymmetric* about

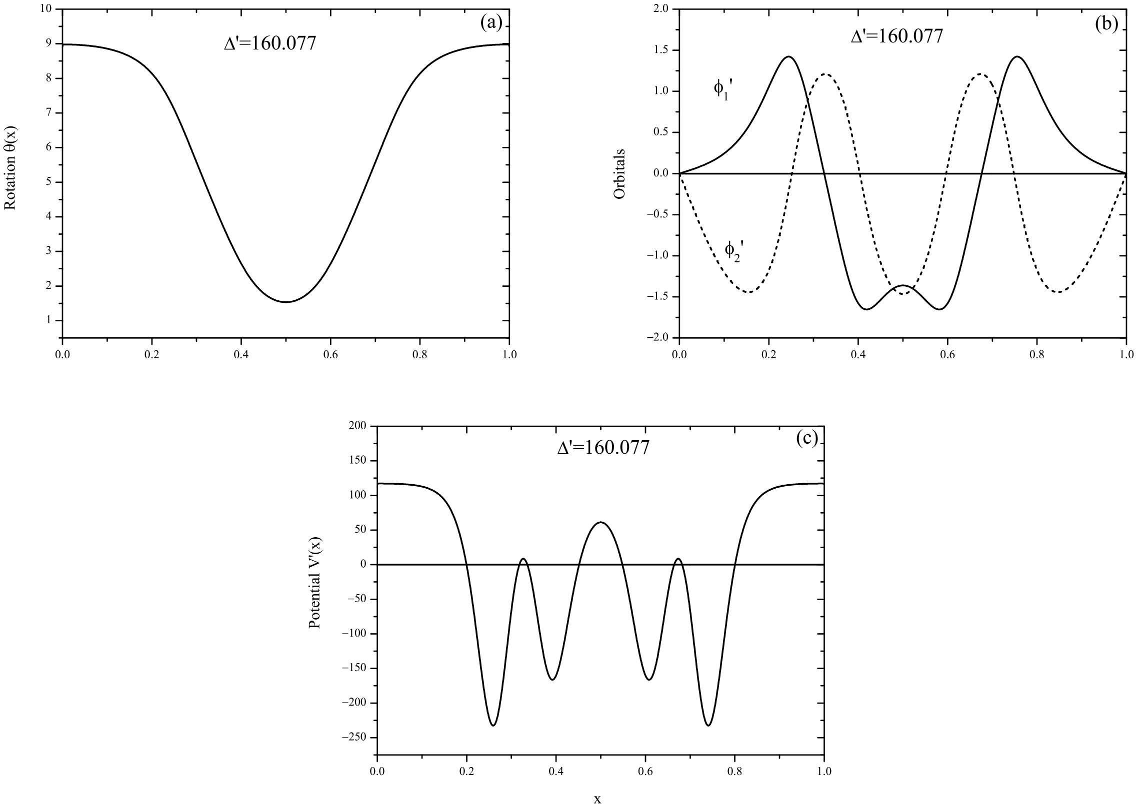

FIG. 5: The functions for (a) the rotation $\theta(x)$; (b) the orbitals $\phi'_1(x), \phi'_2(x)$; (c) the potential $v'(x)$ for the alternate physical system for an eigenvalue difference $\Delta' = \epsilon'_2 - \epsilon'_1 = 160.077$. Observe, Fig. 5b, the configuration of the fermions is 3-5. The original system is the second excited triplet state of configuration 1-3.

$x = 1/2$. Furthermore, the structure of this potential close to and at the boundary is not provided. In addition, the magnitude of the value of the potential given near each boundary differs.

Our results differ in the following ways. First, as noted above, we find no alternate potential $v'(x)$ for the same 1-3 orbital configuration. (In other words there is no physical solution corresponding to $\Delta' = \Delta = 4\pi^2$ even though there exist a couple of normalized set of orbitals $\phi'_i(x)$. See Fig 3c for $\Delta' = 40$.) Second, all our multiple potentials $v'(x)$ are symmetrical, as are all the orbitals $\phi'_i(x)$, about $x = 1/2$. Third, we provide the exact structure of the potentials $v'(x)$ and orbitals $\phi'_i(x)$ close to and at the boundaries.

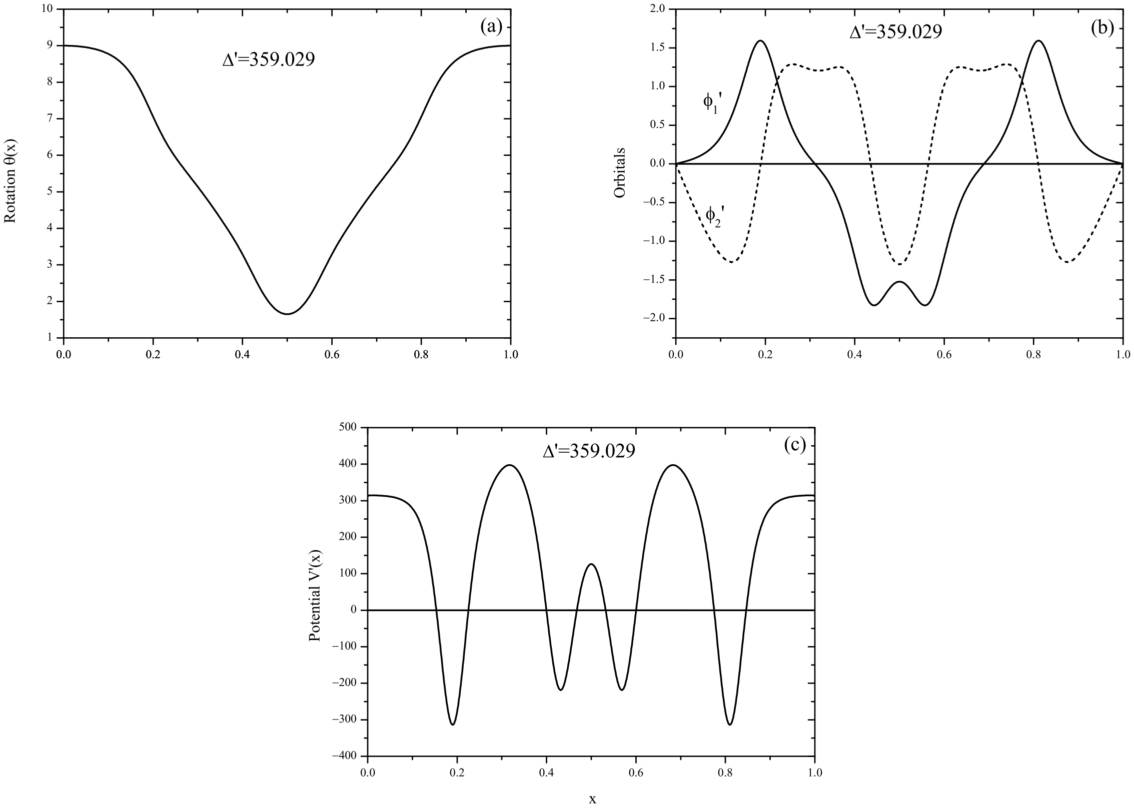

FIG. 6: The same as Fig. 5 but for an eigenvalue difference of $\Delta' = 359.029$. Observe, Fig. 5b, that this too is a 3-5 configuration of the fermions.

V. RESULTS AND DISCUSSION

We conclude by discussing our current understanding of the construction of multiple local potentials $v(\mathbf{r})$ that generate a density $\rho(\mathbf{r})$. In the present work we have considered a system of *noninteracting* fermions in an infinite potential well for which the eigenfunctions and eigenvalues are known. For this system, we have shown the explicit satisfaction of the GL theorem, *i.e.* for the lowest excited triplet state – the lowest excited state of this symmetry – there exists only *one* potential $v(\mathbf{r})$, the original one, that generates the excited state density. For the same system, we have also demonstrated the multiplicity of the potentials for the higher second excited triplet state. The results of these calculations are quite fascinating. First, there exists multiple potentials $v(\mathbf{r})$ with orbital configurations and eigenvalues that *differ* from the original but which generate the density of this excited state. Second, different potentials $v(\mathbf{r})$ with the *same* configuration but *different* eigenvalues also

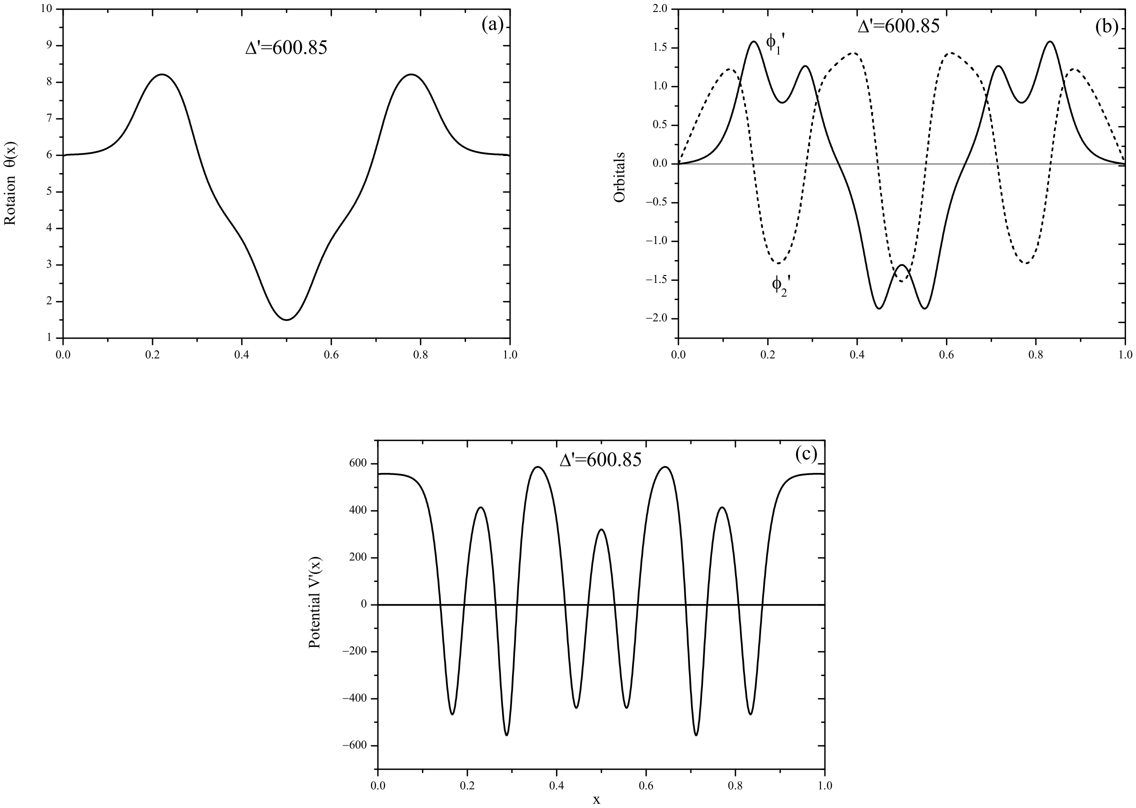

FIG. 7: The same as Fig. 5 but for an eigenvalue difference of $\Delta' = 600.85$. Observe, Fig. 7b, that this is a 3-7 configuration of the fermions.

generate the excited state density. Third, there exists *no other* potential $v(\mathbf{r})$ with the *original* orbital configuration that generates the excited state density.

Consider next a system of *interacting* fermions – electrons – in an external field $\boldsymbol{\mathcal{F}}^{\text{ext}}(\mathbf{r}) = -\nabla v(\mathbf{r})$ and in a ground or excited state. It is possible via QDFT [3, 10] to map such a system to one of a model system of *noninteracting* fermions – the S system – with equivalent density $\rho(\mathbf{r})$. The state or orbital configuration of the S system is *arbitrary*. Thus, the *ground* state of the interacting system can be mapped to an S system that is either in a *ground* or *excited* state. Similarly, the system of electrons in an *excited* state may be mapped to an S system that is in a *ground* or an *excited* state of the same or different configuration. In principle then, in addition to the external potential $v(\mathbf{r})$ of the interacting system, there exist an *infinite* number of local effective potentials $v_s(\mathbf{r})$ that generate a given density $\rho(\mathbf{r})$. Given a density $\rho(\mathbf{r})$, it is also possible to determine [11] via the Zhao-Parr [8] numerical method different local effective potentials that reproduce the density by choosing different orbital configurations. In the mapping from a nondegenerate excited state of the electrons, the constrained-search extension of density functional theory to excited states by Levy-Nagy [12] selects one local potential function $v_s(\mathbf{r})$ with the *same* orbital configuration that will generate the excited state density.

Finally, it is also possible [3, 13–15] to map the interacting system of electrons in a ground or excited state to one of noninteracting bosons in a ground state: the B system. Hence, there exists yet another local effective potential $v_B(\mathbf{r})$ that generates the density of the interacting electrons.

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