

Wigner's $(2n + 1)$ rule for nonlinear Schrödinger equations

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Abstract Wigner's $(2n + 1)$ rule is proven for general total energy functionals, constructed from the expectation value of a linear Hamiltonian and a nonlinear functional of the electron density or of the first order density matrix. Such functionals are common in independent particle models, like the Kohn–Sham density functional or Hartree–Fock theories, but they occur as well in reaction-field type solvent effect models and range-separated hybrid density functional approaches. The fulfillment of the $(2n + 1)$ rule is crucial for the development of efficient perturbation approaches for the treatment of one-electron and two-electron perturbations. A general transformation formula is derived, that removes some of the $(2n + 1)$ -rule violating matrix elements of the perturbation operator from the general expression of the arbitrary order perturbational energy correction of the nonlinear problem.

Keywords Perturbation theory · Nonlinear Schrödinger equation · Density functional theory

1 Introduction

Wigner's $(2n + 1)$ rule (sometimes called as Wigner's $(2n + 1)$ theorem) [1, 2] is widely used in quantum chemistry to simplify higher-order perturbation equations, either in the context of the calculation of higher order properties, or to make more efficient the evaluation of perturbational electron correlation corrections. In many cases one is interested in the perturbational solution of effective nonlinear Schrödinger equations, derived from total energy functionals of the electron density (e.g. Kohn–Sham

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approach) or of the first-order density matrix (e.g. Hartree–Fock theory, density matrix functional theory). Elsewhere, the nonlinearity of the Hamiltonian is related to a physical model, describing e.g. an embedded electronic system, like in various reaction-field type solvent effect theories [3,4]. Recently, we have dealt with a novel category of nonlinear effective Schrödinger equations, arising in the range-separated hybrid density functional framework, where the short-range electron interactions are treated by a density functional, while long-range electron interaction are handled explicitly [5]. By a generalization of the Kohn–Sham theory, which considers the electronic system as an assembly of independent particles, the range-separated framework corresponds to a model system constituted by long-range interacting ensemble of particles. This change of paradigm makes necessary the generalization of earlier formulations of density functional perturbation theory, relying on the independent particle model and adapt the perturbational treatment for more general, many-electron nonlinear Schrödinger equations.

A general demonstration of the validity of Wigner’s theorem for arbitrary variational energy functionals has been given by Gonze [6], who derived useful variation-perturbation equations for Kohn–Sham density functionals as well [7]. This work, widely known in the solid state physicist community, where it is considered as one of the basic references of the density functional perturbation theory (DFPT) [8], seems to have much less influence in the quantum chemistry literature. Independently of Gonze’s work, Wigner’s $(2n + 1)$ theorem has also been invoked in the context of the perturbational solution of nonlinear Schrödinger equations describing solvent effects [9].

In this note an alternative demonstration of the validity of Wigner’s theorem is presented, emphasizing the relationship between the density functional and the effective potential, responsible for the nonlinearity in the effective Hamiltonian. The total energy functional is written as a sum of the Rayleigh-quotient of a linear Hamiltonian plus a general nonlinear functional of the electron density:

$$E = \min_{\Psi \rightarrow N} \left\{ \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} + F[n_\Psi] \right\}. \quad (1)$$

Here \hat{H} is an N -electron, possibly interacting Hamiltonian (not equal to the physical Hamiltonian), $F[n_\Psi]$ is a functional of the total electron density,

$$n_\Psi(\mathbf{r}) = \frac{\langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (2)$$

obtained from the wave function Ψ as the normalized expectation value of the electron density operator, $\hat{n}(\mathbf{r}) = \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i)$.

Applying the variation principle to the total energy functional (1), we have

$$\begin{aligned} \delta E &= \langle \delta \Psi | \hat{H} | \Psi \rangle - \langle \delta \Psi | \Psi \rangle \mathcal{E} + \frac{\delta F[n_\Psi]}{\delta n} \langle \delta \Psi | \hat{n} | \Psi \rangle + \text{c.c.} \\ &= \langle \delta \Psi | \hat{H} | \Psi \rangle - \langle \delta \Psi | \Psi \rangle \mathcal{E} + \langle \delta \Psi | \hat{\Omega}[n_\Psi] | \Psi \rangle + \text{c.c.} = 0, \end{aligned} \quad (3)$$

where the notation “c.c.” means complex conjugate. The last term in this equation has been obtained by the chain rule, taking into account that $\delta n = \langle \delta \Psi | \hat{n} | \Psi \rangle + \langle \Psi | \hat{n} | \delta \Psi \rangle - n_{\Psi} (\langle \delta \Psi | \Psi \rangle + \langle \Psi | \delta \Psi \rangle)$. The effective potential operator, $\hat{\Omega}[n_{\Psi}]$ is defined as

$$\hat{\Omega}[n_{\Psi}] = \int d\mathbf{r} \frac{\delta F[n_{\Psi}]}{\delta n(\mathbf{r})} \hat{n}(\mathbf{r}). \quad (4)$$

Since the variation $\langle \delta \Psi |$ can be arbitrary, the minimizing wave function is supposed to satisfy the following effective Schrödinger equation,

$$(\hat{H} + \hat{\Omega}[n_{\Psi}] - \mathcal{E})|\Psi\rangle = 0. \quad (5)$$

The eigenvalue \mathcal{E} of the nonlinear Schrödinger equation,

$$\mathcal{E} = \frac{\langle \Psi | \hat{H} + \hat{\Omega}[n_{\Psi}] | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (6)$$

differs from the total energy, E , by the double count correction, according to:

$$E = \mathcal{E} - \frac{\langle \Psi | \hat{\Omega}[n_{\Psi}] | \Psi \rangle}{\langle \Psi | \Psi \rangle} + F[n_{\Psi}]. \quad (7)$$

In the following our attention will be focused on the above type of nonlinear time-independent Schrödinger equations, obtained from Eq. 1 by the variation theorem. First a demonstration is given to prove the validity of Wigner’s theorem (Sect. 2), while in Sect. 3 a transformation formula is proposed to get rid of some of the matrix elements that seem to violate the $(2n + 1)$ rule.

2 Wigner’s theorem for nonlinear Schrödinger equations

The generalization of Wigner’s $(2n + 1)$ theorem for total energy functionals of type (1) tells that such a variational total energy functional evaluated with the help of a wave function correct up the n th order of the perturbation is accurate up to terms of order $2n + 1$.

First the case of density functionals will be considered. Then it will be shown that an analogous theorem holds for density matrix functionals as well. The demonstration presented here follows the procedure used in the case of conventional linear Schrödinger equations, as described, in several textbooks, e.g. in Chapter 1.4.1 of Ref. [10].

2.1 Density functionals

The exact variational wave function is expressed with the help of the wave function correct up to order n , denoted by $\Psi^{[n]} = \sum_{\mu=0}^n \lambda^\mu \Psi^{(\mu)}$, as

$$\Psi = \Psi^{[n]} + \chi^{(n+1)}, \quad (8)$$

where $\chi^{(n+1)}$ collects all the remaining terms of order at least of $\mathcal{O}(\lambda^{n+1})$. The value of the total energy functional calculated by $\Psi^{[n]}$ can be obtained as:

$$E[\Psi^{[n]}] = \frac{\langle \Psi^{[n]} | \hat{H} | \Psi^{[n]} \rangle}{\langle \Psi^{[n]} | \Psi^{[n]} \rangle} + F[n_{\Psi^{[n]}}], \quad (9)$$

where $n_{\Psi^{[n]}}(\mathbf{r})$ is the electron density associated with the wave function $\Psi^{[n]}$:

$$\begin{aligned} n_{\Psi^{[n]}}(\mathbf{r}) &= \frac{\langle \Psi^{[n]} | \hat{n}(\mathbf{r}) | \Psi^{[n]} \rangle}{\langle \Psi^{[n]} | \Psi^{[n]} \rangle} = \frac{\langle \Psi - \chi^{(n+1)} | \hat{n} | \Psi - \chi^{(n+1)} \rangle}{\langle \Psi - \chi^{(n+1)} | \Psi - \chi^{(n+1)} \rangle} \\ &= \frac{\langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle}{\langle \Psi | \Psi \rangle} \left(1 + \frac{\langle \Psi | \chi^{(n+1)} \rangle + \langle \chi^{(n+1)} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right) \\ &\quad - \frac{\langle \chi^{(n+1)} | \hat{n}(\mathbf{r}) | \Psi \rangle + \langle \Psi | \hat{n}(\mathbf{r}) | \chi^{(n+1)} \rangle}{\langle \Psi | \Psi \rangle} + \mathcal{O}(\lambda^{2n+2}). \end{aligned} \quad (10)$$

The normalized expectation value of the Hamiltonian can be expanded in an analogous manner as:

$$\begin{aligned} \frac{\langle \Psi^{[n]} | \hat{H} | \Psi^{[n]} \rangle}{\langle \Psi^{[n]} | \Psi^{[n]} \rangle} &= \frac{\langle \Psi - \chi^{(n+1)} | \hat{H} | \Psi - \chi^{(n+1)} \rangle}{\langle \Psi - \chi^{(n+1)} | \Psi - \chi^{(n+1)} \rangle} \\ &= \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \left(1 + \frac{\langle \Psi | \chi^{(n+1)} \rangle + \langle \chi^{(n+1)} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right) \\ &\quad - \frac{\langle \chi^{(n+1)} | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H} | \chi^{(n+1)} \rangle}{\langle \Psi | \Psi \rangle} + \mathcal{O}'(\lambda^{2n+2}). \end{aligned} \quad (11)$$

We need also the series expansion of the density functional, $F[n_{\Psi^{[n]}}]$ around its value corresponding to the exact density, $F[n_\Psi]$,

$$\begin{aligned} F[n_{\Psi^{[n]}}] &= F[n_\Psi + \Delta n] = F[n_\Psi] + \int d\mathbf{r} \frac{\delta F}{\delta n(\mathbf{r})} \Delta n(\mathbf{r}) \\ &\quad + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\delta^2 F}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \Delta n(\mathbf{r}) \Delta n(\mathbf{r}') + \dots, \end{aligned} \quad (12)$$

where the density shift, $\Delta n(\mathbf{r})$ is defined as

$$\Delta n(\mathbf{r}) = \frac{\langle \chi^{(n+1)} | n_\Psi(\mathbf{r}) - \hat{n}(\mathbf{r}) | \Psi \rangle + \langle \Psi | n_\Psi(\mathbf{r}) - \hat{n}(\mathbf{r}) | \chi^{(n+1)} \rangle}{\langle \Psi | \Psi \rangle} + \mathcal{O}(\lambda^{2n+2}). \tag{13}$$

Substituting these expansions in Eq. 9 and using the definition Eq. 4 of the operator $\hat{\Omega}$, the total energy calculated with the wave function correct up to the n th order becomes

$$\begin{aligned} E[n_{\Psi^{[n]}}] &= \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} + F[n_\Psi] \\ &\quad - \langle \Psi | \hat{H} + \hat{\Omega}[n_\Psi] - \mathcal{E} | \chi^{(n+1)} \rangle - \langle \chi^{(n+1)} | \hat{H} + \hat{\Omega}[n_\Psi] - \mathcal{E} | \Psi \rangle \\ &\quad + \mathcal{O}(\lambda^{2n+2}) + \mathcal{O}'(\lambda^{2n+2}), \end{aligned} \tag{14}$$

where the quantity \mathcal{E} has been defined in Eq. 6.

As the exact wave function, Ψ , satisfies the effective Schrödinger equation, Eq. 5, it follows that

$$E[n_{\Psi^{[n]}}] = E[n_\Psi] + \mathcal{O}''(\lambda^{2n+2}). \tag{15}$$

It means that the errors of the variational energy functional calculated with the n th order wave function are at least of order $(2n + 2)$, and by consequence it can be concluded that the knowledge of the wave function up to order n is sufficient to provide the total energy correct up to the order $(2n + 1)$.

2.2 Generalization for density matrix functionals

Let us consider that the total energy is a functional of the first order density matrix, according to

$$E = \min_{\Psi \rightarrow N} \left\{ \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} + F[\gamma_\Psi] \right\}, \tag{16}$$

where $\gamma_\Psi(\mathbf{r}, \mathbf{r}')$ is defined as

$$\gamma_\Psi(\mathbf{r}, \mathbf{r}') = \frac{\langle \Psi | \hat{\gamma}(\mathbf{r}, \mathbf{r}') | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{17}$$

with $\hat{\gamma}(\mathbf{r}, \mathbf{r}')$, the first order density matrix operator.

The corresponding effective Schrödinger equation is

$$\delta E = \langle \delta \Psi | \hat{H} | \Psi \rangle - \langle \delta \Psi | \Psi \rangle \mathcal{E} + \langle \delta \Psi | \hat{\Lambda}[\gamma_\Psi] | \Psi \rangle + \text{c.c.} = 0 \tag{18}$$

where the effective potential operator $\hat{\Lambda}[\gamma_\Psi]$ is defined through the functional derivative of the density matrix functional,

$$\hat{\Lambda}[\gamma_\Psi] = \iint d\mathbf{r} d\mathbf{r}' \frac{\delta F[\gamma_\Psi]}{\delta \gamma(\mathbf{r}, \mathbf{r}')} \hat{\gamma}(\mathbf{r}, \mathbf{r}'). \quad (19)$$

In contrast to the density functional theory, where the effective potential is local, $\hat{\Lambda}[\gamma_\Psi]$ is defined through a nonlocal potential kernel, given formally as [11]

$$w(\mathbf{r}, \mathbf{r}') = \frac{\delta F[\gamma_\Psi]}{\delta \gamma(\mathbf{r}, \mathbf{r}')}. \quad (20)$$

In some sense, the Hartree–Fock exchange functional can be regarded as a simple example of a density matrix functional, which is quadratic in $\gamma(\mathbf{r}; \mathbf{r}')$:

$$E_x^{HF}[\gamma_\Psi] = -\frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{|\gamma_\Psi(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}, \quad (21)$$

and the corresponding effective exchange potential operator is

$$\hat{\Lambda}_x^{HF}[\gamma_\Psi] = - \iint d\mathbf{r} d\mathbf{r}' \frac{\gamma_\Psi^*(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \hat{\gamma}(\mathbf{r}, \mathbf{r}'). \quad (22)$$

Applying analogous manipulations on the Hartree energy functional (of the density), one retrieves the well-known expression of the complete Hartree–Fock effective potential. In the more interesting case of the density matrix functional theory (DMFT), a nonlocal potential, functional derivative of the density matrix functional describing correlation effects, can be written in terms of the natural orbitals and their occupation numbers, as shown recently by Pernal [12].

Following similar steps as in Sect. 2.1, it is easy to demonstrate that Wigner's theorem applies to the density matrix functionals as well,

$$E[\gamma_{\Psi[n]}] = E[\gamma_\Psi] + \mathcal{O}(\lambda^{2n+2}). \quad (23)$$

This is a general result which can be used not only in the well-documented case of Hartree–Fock perturbation theory, but might turn out to be useful in perturbation theory applied to nonlinear effective Hamiltonian operators obtained in a DMFT framework [13, 14].

3 Transformation of $(2n + 1)$ -rule violating matrix elements

Coming back to the case of density functionals, one might wish to solve the effective nonlinear Schrödinger equation by perturbation methods. After having expanded the

energy, the potential operator and the wave function in power series of a perturbation parameter, λ , one can write down the following p -th order Schrödinger equation [15]:

$$\{\hat{H}^{(0)} + \hat{\Omega}^{(0)} - \mathcal{E}^{(0)}\}|\Psi^{(k)}\rangle + \hat{W}|\Psi^{(k-1)}\rangle = \sum_{\nu=0}^{k-1} \{\mathcal{E}^{(k-\nu)} - \hat{\Omega}^{(k-\nu)}\}|\Psi^{(\nu)}\rangle. \tag{24}$$

The p -th order eigenvalue correction is obtained by multiplication with $\langle\Psi^{(0)}|$ followed by integration. Using the intermediate normalization condition, $\langle\Psi^{(0)}|\Psi^{(j)}\rangle = 0$ for $\forall j > 0$, one has

$$\mathcal{E}^{(p)} = \langle\Psi^{(0)}|\hat{W}|\Psi^{(p-1)}\rangle + \sum_{\tau=1}^p \langle\Psi^{(0)}|\hat{\Omega}^{(\tau)}|\Psi^{(p-\tau)}\rangle. \tag{25}$$

Setting the density functional to zero one gets back, as expected, the conventional RSPT energy correction as $E^{(p)} = \langle\Psi^{(0)}|\hat{W}|\Psi^{(p-1)}\rangle$. Since this expression seems to be in contradiction with Wigner’s theorem, several authors have elaborated algebraic approaches consisting in a series of manipulations to transform the general energy correction formula [16–20]. The alternative forms thus obtained, make possible to take computational advantage of Wigner’s theorem and avoid dealing with higher than n -th order wave function corrections to obtain the energy of $2n$ or $2n + 1$ order.

In the case of the usual Rayleigh-Schrödinger perturbation theory (RSPT) applied to a linear Schrödinger equation, the transformation rules have been given to remove matrix elements of type $\langle\Psi^{(0)}|\hat{W}|\Psi^{(p)}\rangle$ and transform them to $\langle\Psi^{(k)}|\hat{W}|\Psi^{(p-k)}\rangle$, where $2k = p$ or $2k + 1 = p$. Some of the authors used the intermediate (or correlation) normalization condition, i.e. $\langle\Psi^{(0)}|\Psi^{(j)}\rangle = 0$ for $\forall j; j > 0$ [16–19], while others derived analogous turnover transformations [20] using different normalization conventions, which consists in $\sum_{k=0}^n \langle\Psi^{(k)}|\Psi^{(n-k)}\rangle = 0 \quad \forall n; n > 0$. This latter normalization convention has been adopted in the more recent works of Gonze [7].

We shall suppose that the Hamiltonian as well as the perturbation \hat{W} and the potential $\hat{\Omega}$ operators are hermitian, the wave function is real and normalized according to the above defined correlation (or intermediate) normalization convention. In a first step, a general transformation relationship will be obtained by the algebraic manipulation of the general order Schrödinger equation. Application of Eq. 24 at the $(p - j + 1)$ -th order and multiplication by $\langle\Psi^{(j)}|$ leads to

$$\begin{aligned} \langle\Psi^{(j)}|\hat{H}^{(0)} + \hat{\Omega}^{(0)} - \mathcal{E}^{(0)}|\Psi^{(p-j+1)}\rangle &= -\langle\Psi^{(j)}|\hat{W}|\Psi^{(p-j)}\rangle \\ &+ \sum_{\nu=0}^{p-j} \langle\Psi^{(j)}|\mathcal{E}^{(p-j+1-\nu)} - \hat{\Omega}^{(p-j+1-\nu)}|\Psi^{(\nu)}\rangle. \end{aligned} \tag{26}$$

By interchanging the role of indices $(p - j + 1)$ and j one obtains similarly

$$\begin{aligned} \langle \Psi^{(p-j+1)} | \hat{H}^{(0)} + \hat{\Omega}^{(0)} - \mathcal{E}^{(0)} | \Psi^{(j)} \rangle &= -\langle \Psi^{(p-j+1)} | \hat{W} | \Psi^{(j-1)} \rangle \\ &+ \sum_{\mu=0}^{j-1} \langle \Psi^{(p-j+1)} | \mathcal{E}^{(j-\mu)} - \hat{\Omega}^{(j-\mu)} | \Psi^{(\mu)} \rangle. \end{aligned} \quad (27)$$

Using the hermiticity of the zeroth order Hamiltonian as well as that of the perturbation \hat{W} and potential $\hat{\Omega}$ operators, one arrives to the basic transformation formula:

$$\begin{aligned} \langle \Psi^{(j-1)} | \hat{W} | \Psi^{(p+1-j)} \rangle &= \langle \Psi^{(j)} | \hat{W} | \Psi^{(p-j)} \rangle \\ &+ \sum_{\mu=0}^{j-1} \langle \Psi^{(p+1-j)} | \mathcal{E}^{(j-\mu)} - \hat{\Omega}^{(j-\mu)} | \Psi^{(\mu)} \rangle \\ &- \sum_{\nu=0}^{p-j} \langle \Psi^{(j)} | \mathcal{E}^{(p+1-j-\nu)} - \hat{\Omega}^{(p+1-j-\nu)} | \Psi^{(\nu)} \rangle. \end{aligned} \quad (28)$$

A general turnover rule can be derived by the iterative application of Eq. 28, starting from the perturbation operator matrix element $\langle \Psi^{(0)} | \hat{W} | \Psi^{(p)} \rangle$. By successive substitutions it is easy to see that

$$\begin{aligned} \langle \Psi^{(0)} | \hat{W} | \Psi^{(p)} \rangle &= \langle \Psi^{(1)} | \hat{W} | \Psi^{(p-1)} \rangle + T(1, p) \\ &= \langle \Psi^{(2)} | \hat{W} | \Psi^{(p-2)} \rangle + T(1, p) + T(2, p) \\ &= \dots \dots \dots \\ &= \langle \Psi^{(m)} | \hat{W} | \Psi^{(p-m)} \rangle + \sum_{j=1}^m T(j, p), \end{aligned} \quad (29)$$

where the increment $T(j, p)$ has been defined as

$$\begin{aligned} T(j, p) &= \sum_{\mu=0}^{j-1} \langle \Psi^{(p+1-j)} | \mathcal{E}^{(j-\mu)} - \hat{\Omega}^{(j-\mu)} | \Psi^{(\mu)} \rangle \\ &- \sum_{\nu=0}^{p-j} \langle \Psi^{(j)} | \mathcal{E}^{(p+1-j-\nu)} - \hat{\Omega}^{(p+1-j-\nu)} | \Psi^{(\nu)} \rangle. \end{aligned} \quad (30)$$

The final turnover expression is looked for as

$$\langle \Psi^{(0)} | \hat{W} | \Psi^{(p)} \rangle = \langle \Psi^{(m)} | \hat{W} | \Psi^{(p-m)} \rangle + S(m, p), \quad (31)$$

$$S(m, p) = \sum_{j=1}^m T(j, p) \quad (32)$$

where one would like to bring $S(m, p)$ to the simplest possible form.

The first order relationship is readily obtained:

$$S(1, p) = \langle \Psi^{(p)} | \mathcal{E}^{(1)} - \hat{\Omega}^{(1)} | \Psi^{(0)} \rangle - \sum_{\nu=0}^{p-1} \langle \Psi^{(1)} | \mathcal{E}^{(p-\nu)} - \hat{\Omega}^{(p-\nu)} | \Psi^{(\nu)} \rangle. \quad (33)$$

The second order expression contains several terms, namely

$$\begin{aligned} S(2, p) = & \langle \Psi^{(p)} | \mathcal{E}^{(1)} - \hat{\Omega}^{(1)} | \Psi^{(0)} \rangle - \sum_{\nu=0}^{p-1} \langle \Psi^{(1)} | \mathcal{E}^{(p-\nu)} - \hat{\Omega}^{(p-\nu)} | \Psi^{(\nu)} \rangle \\ & + \langle \Psi^{(p-1)} | \mathcal{E}^{(2)} - \hat{\Omega}^{(2)} | \Psi^{(0)} \rangle + \langle \Psi^{(p-1)} | \mathcal{E}^{(1)} - \hat{\Omega}^{(1)} | \Psi^{(1)} \rangle \\ & - \sum_{\nu=0}^{p-2} \langle \Psi^{(2)} | \mathcal{E}^{(p-1-\nu)} - \hat{\Omega}^{(p-1-\nu)} | \Psi^{(\nu)} \rangle. \end{aligned} \quad (34)$$

The second term of Eq. 34 can be transformed as

$$\begin{aligned} & \sum_{\nu=0}^{p-1} \langle \Psi^{(1)} | \mathcal{E}^{(p-\nu)} - \hat{\Omega}^{(p-\nu)} | \Psi^{(\nu)} \rangle = \\ & \sum_{\nu=0}^{p-2} \langle \Psi^{(1)} | \mathcal{E}^{(p-\nu)} - \hat{\Omega}^{(p-\nu)} | \Psi^{(\nu)} \rangle + \langle \Psi^{(1)} | \mathcal{E}^{(1)} - \hat{\Omega}^{(1)} | \Psi^{(p-1)} \rangle \end{aligned} \quad (35)$$

leading to a cancelation between $\langle \Psi^{(1)} | \mathcal{E}^{(1)} - \hat{\Omega}^{(1)} | \Psi^{(p-1)} \rangle$ and $\langle \Psi^{(p-1)} | \mathcal{E}^{(1)} - \hat{\Omega}^{(1)} | \Psi^{(1)} \rangle$. Regrouping the remainder in two sums, one obtains immediately

$$\begin{aligned} S(2, p) = & \sum_{j=1}^2 \langle \Psi^{(p+1-j)} | \mathcal{E}^{(j)} - \hat{\Omega}^{(j)} | \Psi^{(0)} \rangle \\ & - \sum_{j=1}^2 \sum_{\nu=0}^{p-2} \langle \Psi^{(j)} | \mathcal{E}^{(p+1-j-\nu)} - \hat{\Omega}^{(p+1-j-\nu)} | \Psi^{(\nu)} \rangle. \end{aligned} \quad (36)$$

Based on this second order result, one can attempt the following generalization for an arbitrary order m :

$$\begin{aligned} S(m, p) = & \sum_{j=1}^m \langle \Psi^{(p+1-j)} | \mathcal{E}^{(j)} - \hat{\Omega}^{(j)} | \Psi^{(0)} \rangle \\ & - \sum_{j=1}^m \sum_{\nu=0}^{p-m} \langle \Psi^{(j)} | \mathcal{E}^{(p+1-j-\nu)} - \hat{\Omega}^{(p+1-j-\nu)} | \Psi^{(\nu)} \rangle. \end{aligned} \quad (37)$$

The above expression is of course valid for $m = 1$ and $m = 2$. Its general validity for $m < p$ will be proven by induction, i.e. by showing that, starting from the m -th order

relationship and adding the increment $T(m + 1, p)$, one arrives to $S(m + 1, p)$, i.e. the $(m + 1)$ -th order turnover transformation formula.

The sum of $T(m + 1, p)$ and $S(m, p)$ is

$$\begin{aligned}
 S(m, p) + T(m + 1, p) &= \sum_{j=1}^m \langle \Psi^{(p+1-j)} | \mathcal{E}^{(j)} - \hat{\Omega}^{(j)} | \Psi^{(0)} \rangle \\
 &\quad - \sum_{j=1}^m \sum_{v=0}^{p-m} \langle \Psi^{(j)} | \mathcal{E}^{(p+1-j-v)} - \hat{\Omega}^{(p+1-j-v)} | \Psi^{(v)} \rangle \\
 &\quad + \sum_{v=0}^m \langle \Psi^{(p-m)} | \mathcal{E}^{(m+1-v)} - \hat{\Omega}^{(m+1-v)} | \Psi^{(v)} \rangle \\
 &\quad - \sum_{v=0}^{p-m-1} \langle \Psi^{(m+1)} | \mathcal{E}^{(p-m-v)} - \hat{\Omega}^{(p-m-v)} | \Psi^{(v)} \rangle. \quad (38)
 \end{aligned}$$

Separate the upper limit $v = p - m$ in the second sum and change the lower summation limit from $v = 1$ to $v = 0$ to obtain

$$\begin{aligned}
 &\sum_{j=1}^m \sum_{v=0}^{p-m} \langle \Psi^{(j)} | \mathcal{E}^{(p+1-j-v)} - \hat{\Omega}^{(p+1-j-v)} | \Psi^{(v)} \rangle \\
 &= \sum_{j=1}^m \sum_{v=0}^{p-m-1} \langle \Psi^{(j)} | \mathcal{E}^{(p+1-j-v)} - \hat{\Omega}^{(p+1-j-v)} | \Psi^{(v)} \rangle \\
 &\quad + \sum_{j=0}^m \langle \Psi^{(j)} | \mathcal{E}^{(m+1-v)} - \hat{\Omega}^{(m+1-v)} | \Psi^{(p-m)} \rangle \\
 &\quad - \langle \Psi^{(0)} | \mathcal{E}^{(m+1)} - \hat{\Omega}^{(m+1)} | \Psi^{(p-m)} \rangle, \quad (39)
 \end{aligned}$$

which allows us to simplify Eq. 38 as

$$\begin{aligned}
 S(m, p) + T(m + 1, p) &= \sum_{j=1}^m \langle \Psi^{(p+1-j)} | \mathcal{E}^{(j)} - \hat{\Omega}^{(j)} | \Psi^{(0)} \rangle \\
 &\quad - \sum_{j=1}^m \sum_{v=0}^{p-m-1} \langle \Psi^{(j)} | \mathcal{E}^{(p+1-j-v)} - \hat{\Omega}^{(p+1-j-v)} | \Psi^{(v)} \rangle \\
 &\quad + \langle \Psi^{(0)} | \mathcal{E}^{(m+1)} - \hat{\Omega}^{(m+1)} | \Psi^{(p-m)} \rangle \\
 &\quad - \sum_{v=0}^{p-m-1} \langle \Psi^{(m+1)} | \mathcal{E}^{(p-m-v)} - \hat{\Omega}^{(p-m-v)} | \Psi^{(v)} \rangle. \quad (40)
 \end{aligned}$$

After merging the terms in a single and a double sum, one arrives to the expression

$$\begin{aligned}
 S(m, p) + T(m + 1, p) &= \sum_{j=1}^m \langle \Psi^{(p+1-j)} | \mathcal{E}^{(j)} - \hat{\Omega}^{(j)} | \Psi^{(0)} \rangle \\
 &+ \langle \Psi^{(0)} | \mathcal{E}^{(m+1)} - \hat{\Omega}^{(m+1)} | \Psi^{(p+1-(m+1))} \rangle \\
 &- \sum_{j=1}^m \sum_{v=0}^{p-(m+1)} \langle \Psi^{(j)} | \mathcal{E}^{(p+1-j-v)} - \hat{\Omega}^{(p+1-j-v)} | \Psi^{(v)} \rangle \\
 &- \sum_{v=0}^{p-(m+1)} \langle \Psi^{(m+1)} | \mathcal{E}^{(p+1-(m+1)-v)} - \hat{\Omega}^{(p+1-(m+1)-v)} | \Psi^{(v)} \rangle, \tag{41}
 \end{aligned}$$

which is obviously equal to $S(m + 1, p)$:

$$\begin{aligned}
 S(m, p) + T(m + 1, p) &= \sum_{j=1}^{m+1} \langle \Psi^{(p+1-j)} | \mathcal{E}^{(j)} - \hat{\Omega}^{(j)} | \Psi^{(0)} \rangle \\
 &- \sum_{j=1}^{m+1} \sum_{v=0}^{p-(m+1)} \langle \Psi^{(j)} | \mathcal{E}^{(p+1-j-v)} - \hat{\Omega}^{(p+1-j-v)} | \Psi^{(v)} \rangle \\
 &= S(m + 1, p). \tag{42}
 \end{aligned}$$

Thus, with the help of the general turnover relationship Eq. 37 one could get rid of those matrix elements of the perturbation operator, \hat{W} , that seem to violate Wigner’s theorem. Still, there remain terms which require the knowledge of wave function corrections that are higher order than permitted by the $(2n + 1)$ theorem. Such terms are going to be canceled by analogous ones in the series expansion of the double count correction.

Remark that a slightly different, alternative form of the turnover transformation can be obtained by grouping together all the contributions that contain the zeroth order wave function. By the virtue of the intermediate normalization condition, the eigenvalue corrections occurring in combination with the matrix elements $\langle \Psi^{(j)} | \Psi^{(0)} \rangle$ vanish and one gets:

$$\begin{aligned}
 S(m, p) &= \sum_{j=1}^m \left(\langle \Psi^{(j)} | \hat{\Omega}^{(p+1-j)} | \Psi^{(0)} \rangle - \langle \Psi^{(p+1-j)} | \hat{\Omega}^{(j)} | \Psi^{(0)} \rangle \right) \\
 &- \sum_{j=1}^m \sum_{v=1}^{p-m} \langle \Psi^{(j)} | \mathcal{E}^{(p+1-j-v)} - \hat{\Omega}^{(p+1-j-v)} | \Psi^{(v)} \rangle. \tag{43}
 \end{aligned}$$

Substituting this result in the general eigenvalue correction and setting $p = 2n$ or $p = 2n + 1$ and $m = n$, the $2n$ and $2n + 1$ order eigenvalue corrections are found to be

$$\begin{aligned} \mathcal{E}^{(2n)} &= \langle \Psi^{(n)} | \hat{W} | \Psi^{(n-1)} \rangle \\ &+ \sum_{j=1}^n \langle \Psi^{(j)} | \hat{\Omega}^{(2n-j)} | \Psi^{(0)} \rangle + \sum_{j=n+1}^{2n} \langle \Psi^{(2n-j)} | \hat{\Omega}^{(j)} | \Psi^{(0)} \rangle \\ &- \sum_{j=1}^n \sum_{v=1}^{n-1} \langle \Psi^{(j)} | \mathcal{E}^{(2n-j-v)} - \hat{\Omega}^{(2n-j-v)} | \Psi^{(v)} \rangle \end{aligned} \quad (44)$$

and

$$\begin{aligned} \mathcal{E}^{(2n+1)} &= \langle \Psi^{(n)} | \hat{W} | \Psi^{(n)} \rangle \\ &+ \sum_{j=1}^n \langle \Psi^{(j)} | \hat{\Omega}^{(2n+1-j)} | \Psi^{(0)} \rangle + \sum_{j=n+1}^{2n+1} \langle \Psi^{(2n+1-j)} | \hat{\Omega}^{(j)} | \Psi^{(0)} \rangle \\ &- \sum_{j=1}^n \sum_{v=1}^n \langle \Psi^{(j)} | \mathcal{E}^{(2n+1-j-v)} - \hat{\Omega}^{(2n+1-j-v)} | \Psi^{(v)} \rangle. \end{aligned} \quad (45)$$

After changing the summation variable $k = j - (n + 1)$ in the second sum we obtain a further variant, namely

$$\begin{aligned} \mathcal{E}^{(2n)} &= \langle \Psi^{(n)} | \hat{W} | \Psi^{(n-1)} \rangle \\ &+ \sum_{j=1}^n \langle \Psi^{(j)} | \hat{\Omega}^{(2n-j)} | \Psi^{(0)} \rangle + \sum_{k=0}^{n-1} \langle \Psi^{(n-1-k)} | \hat{\Omega}^{(n+1+k)} | \Psi^{(0)} \rangle \\ &- \sum_{j=1}^n \sum_{v=1}^{n-1} \langle \Psi^{(j)} | \mathcal{E}^{(2n-j-v)} - \hat{\Omega}^{(2n-j-v)} | \Psi^{(v)} \rangle. \end{aligned} \quad (46)$$

and

$$\begin{aligned} \mathcal{E}^{(2n+1)} &= \langle \Psi^{(n)} | \hat{W} | \Psi^{(n)} \rangle \\ &+ \sum_{j=1}^n \langle \Psi^{(j)} | \hat{\Omega}^{(2n+1-j)} | \Psi^{(0)} \rangle + \sum_{k=0}^n \langle \Psi^{(n-k)} | \hat{\Omega}^{(n+1+k)} | \Psi^{(0)} \rangle \\ &- \sum_{j=1}^n \sum_{v=1}^n \langle \Psi^{(j)} | \mathcal{E}^{(2n+1-j-v)} - \hat{\Omega}^{(2n+1-j-v)} | \Psi^{(v)} \rangle. \end{aligned} \quad (47)$$

As to now, no explicit algebraic rule has been found to take full advantage from the cancelation of all the $(2n + 1)$ rule violating matrix elements, warranted, in principle, by Wigner's theorem. Such a cancelation should be revealed on a case-by-case basis, working out algebraically the individual terms [15].

4 Conclusions and perspectives

Wigner's theorem is of central importance in perturbation theory, therefore it is essential to verify its validity and understand the way it is fulfilled in the case of nonlinear Schrödinger equations. Following the work of Gonze, the role of Wigner's theorem has been widely recognized in the context of DFPT [21–24]. Our recent work on London dispersion forces [25] has shown that Wigner's theorem simplifies considerably the 2nd order correlation energy expression for nonlinear Hamiltonian operators as well.

In this work a generalization of the turnover transformation for the perturbational corrections to the eigenvalues of a nonlinear Schrödinger equation was presented too. Contrary to the linear case, there remain some “irregular” matrix elements, involving the potential operator $\hat{\Omega}$, which are supposed to be canceled by analogous terms of the series expansion of the double count correction. Lacking a general formula for this latter case, such cancelations should be worked out on a case-by-case basis. In fact, the turnover formula has been recently applied to elaborate RSPT energy corrections [15], which could be obtained independently in a variation-perturbation context [26]. For the time being only total energy corrections up to fourth order has been elaborated individually. Although from the viewpoint of practical applications this seems to be amply sufficient it might be interesting in the future to work out a complete algebraic treatment of the perturbation expansion of the *total energy* for arbitrary order as well.

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