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Dilatation transformation and sum rules for general potentials including self-consistent field potentials

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Abstract. The eigenfunctions and energies of general dilated Hamiltonians are expanded in powers of the dilatation parameter. These expansions, augmented by stationarity and stability conditions, are used to derive exact sum rules for bound and resonance states. Particular attention is paid to Hamiltonians with potentials which depend on external parameters, such as the nuclear coordinates in molecules, and to self-consistent potentials. The sum rules can be employed in practical computations to improve the quality of the results and may also serve in analyzing the results from approximate calculations.

Key words: Dilatation transformation – Sum rules

1 Introduction

Over the past several years, extensive research has been devoted to the development of computational methods for the determination of resonance energies and widths of both atomic and molecular systems. Among the most notable of these approaches are those based on dilatation transformations [1–3]. One of the most attractive features of this approach is the relative ease with which standard programs of quantum chemistry can be modified to include also non-stationary systems such as autoionizing states, electron scattering resonances (both shape and core-excited) and, in certain versions of the theory, Auger type resonances. The availability of exact numerical relations such as the complex virial theorem [4–6] and higher order sum-rules [7, 8] proved useful for both the understanding and the computational application of the method. These relations are now regarded as valuable tools to tame numerical instabilities that are introduced by deficiencies of the finite basis sets used in resonance calculations.

Another development in the theory of dilatation transformation is the obvious generalization of conventional self-consistent field theory (SCF) to its complex version (CSCF). In CSCF approaches one starts from an already dilated Hamiltonian operator. The complex equations for resonance energies are then derived

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invoking essentially the same variational arguments used to derive the bound state SCF equations. For instance, for the complex energy corresponding to an atomic shape resonance, trial wavefunctions using single Slater determinants consisting of the spin orbitals of, e.g., a closed shell target system plus one outer orbital have been used successfully [9–11]. The CSCF equations are then obtained by requiring stationarity of the energy functional with respect to the variations of the orbitals. The energy functional differs from the one used in conventional bound state calculations essentially in two respects. The first is the use of biorthogonal scalar products and the second is the complex nature of the Lagrange multipliers. As in standard SCF approaches, the latter serve to satisfy orthonormality constraints for the orbitals. The CSCF data may also serve as input data for dilated electron propagator calculations [12].

In the present work we formulate the perturbation theory describing the dependence of resonance energies and wavefunctions on the dilatation angle Θ. The perturbation expansion also serves in the derivation of the general virial theorem as well as of higher order sum rules.

In section 2 the method for treating general Hamiltonians with a dilatation analytic potential [13] is discussed. In Sect. 3 the theory is made specific to the Coulomb potential. Here, we first discuss briefly the atomic case, for which sum rules have been derived previously [5], and then focus attention on the molecular case for which the theory of Sect. 2 has been extended to accommodate the constraints introduced by a set of external parameters (the nuclear coordinates). Finally, in Sect. 4, we generalize the approach to the more involved situation of self-consistent potentials.

Obtaining exact sum rules for general potentials is the main focus of the present paper. Since the method of derivation is relatively straightforward, it can be presented here in a form suitable for readers who are unfamiliar with the topic of complex rotation. In principle, the sum rules may be useful in the numerical calculation of resonance energies and widths within the framework of complex rotations. This aspect is only touched upon in this paper (see Sect. 5).

It is usually assumed that the identification of resonances with the complex energy values obtained from the CSCF variation is correct because it is apparently a natural extension of the situation encountered for certain types of potentials which are classified as dilatation analytic. One of the fundamental properties of such potentials is that their spectrum may contain complex eigenvalues which are independent of the dilatation parameter Θ once they are "uncovered" (in the usual geometric visualization with the Θ-dependent continuum cut fanning out into the lower half of the complex plane). This Θ independence of the CSCF solutions may not be true generally [14] as is discussed briefly in Sects. 4 and 5.

2 Theory for General Potentials

In this section we present the general expressions of a perturbation theory for unspecified potentials in terms of the dilatation parameter Θ which is assumed real valued. In the following sections the obtained relations will be presented explicitly for the Coulomb and the Hartree–Fock potentials for a system interacting by Coulomb forces.

Throughout this paper we will indicate dilated quantities such as operators, eigenfunctions, and eigenvalues by script letters (e.g. $\mathscr{H}$, $\mathscr{f}(\mathscr{r})$, $\mathscr{E}$) and undilated quantities in straight notation (e.g. H, $f(r)$, E). Hence, the dilated Schrödinger equation reads as

$$\mathscr{H}\,|\mathscr{n}\rangle = \mathscr{E}_n\,|\mathscr{n}\rangle, \tag{2.1}$$

with $\mathscr{H} = Te^{-2i\Theta} + \mathscr{v}$. T is the original undilated kinetic energy operator. The dilated, general potential function $\mathscr{v}$ is obtained from the original potential function V by replacing all position vectors $\boldsymbol{r}$ by $\boldsymbol{r}\,e^{i\Theta}$. We partition the dilated Hamiltonian as

$$\mathscr{H} = H + \mathscr{U} = H + [(e^{-2i\Theta} - 1)\,T + (\mathscr{v} - V)] \tag{2.2}$$

and expand $\mathscr{H}$ in powers of $i\Theta$:

$$\mathscr{H} = H + \mathscr{U} = H + {}^1U\,i\Theta - {}^2U\,\Theta^2 + \cdots, \tag{2.3}$$

with ${}^1U = -2T - i\left(\frac{\partial \mathscr{v}}{\partial \Theta}\right)_{\Theta=0}$ and ${}^2U = 2T - \frac{1}{2}\left(\frac{\partial^2 \mathscr{v}}{\partial \Theta^2}\right)_{\Theta=0}$.

Left superscripts are used to indicate the order of terms in the expansion. In the same manner we expand the eigenstates of $\mathscr{H}$ as

$$|\mathscr{n}\rangle = |n\rangle + |{}^1n\rangle i\Theta - |{}^2n\rangle\Theta^2 + O(\Theta^3). \tag{2.4}$$

Here we assume that the undilated states $|n\rangle$ are normalized while the dilated states $|\mathscr{n}\rangle$ obey the intermediate normalization $\langle n|\mathscr{n}\rangle = 1$. In the case that normalized dilated orbitals are wanted we can incorporate this by writing

$$|\mathscr{n}\rangle = |n\rangle + |{}^1n\rangle i\Theta - (|{}^2n\rangle - \tfrac{1}{2}|n\rangle\langle {}^1n^*|{}^1n\rangle)\Theta^2 + O(\Theta^3), \tag{2.5}$$

which expresses normalization through second order. The star in the bra-state vectors indicates the biorthogonal scalar product which is required in resonance eigenvalue methods. Further we assume the corrections to the unperturbed state vector to be orthogonal to $|n\rangle$, i.e. $\langle {}^an^*|n\rangle = \langle n|{}^an\rangle = 0$ for $a = 1, 2\,\cdots$.

The complex eigenenergy of $\mathscr{H}$ is defined as

$$\mathscr{E}_n = \frac{\langle \mathscr{n}^*|\mathscr{H}|\mathscr{n}\rangle}{\langle \mathscr{n}^*|\mathscr{n}\rangle}$$

$$= \frac{\langle \mathscr{n}^*|H|\mathscr{n}\rangle}{\langle \mathscr{n}^*|\mathscr{n}\rangle} + \frac{\langle \mathscr{n}^*|\mathscr{U}|\mathscr{n}\rangle}{\langle \mathscr{n}^*|\mathscr{n}\rangle}. \tag{2.6a}$$

It can be expanded in analogy to $\mathscr{H}$ and $|\mathscr{n}\rangle$:

$$\mathscr{E}_n = E_n + i\Theta\,{}^1E_n - \Theta^2\,{}^2E_n + \cdots. \tag{2.6b}$$

The expansion coefficients will be determined below.

If we expand bound states about an undilated solution all corrections $|{}^an\rangle$ are real and the stars in the corresponding bra vectors are redundant. However, one can conceive a similar expansion for resonances in which case one would have to expand about an already dilated solution so that the resonance is "uncovered" in the sense of the Balslev–Combes theory [2]. In this more general case all corrections $|{}^an\rangle$ are intrinsically complex and have to be multiplied by $(i\Theta)^a$ where the parameter Θ is now to be interpreted as an additional dilatation angle, i.e., the expansion is then about the dilated solution $\Theta_0 \neq 0$. For the sake of generality we keep the stars in this paper.

The expectation value of H in the state $|\mathscr{n}\rangle$ is, through second order, given by

$$\begin{aligned}\frac{\langle \mathscr{n}^*|H|\mathscr{n}\rangle}{\langle \mathscr{n}^*|\mathscr{n}\rangle} &= \frac{E_n - \Theta^2\langle {}^1n^*|H|{}^1n\rangle + O(\Theta^3)}{1 - \Theta^2\langle {}^1n^*|{}^1n\rangle + O(\Theta^3)} \\ &= E_n - \Theta^2\langle {}^1n^*|H - E_n|{}^1n\rangle + O(\Theta^3). \end{aligned} \tag{2.7}$$

This equation is universal for all potentials whereas the explicit form of the expectation value of $\mathscr{U}$ depends on the specific potential function of the problem.

In order to obtain a more systematic notation we insert the expansions (2.3), (2.4) and (2.6b) into Schrödinger's equation (2.1). Equating the terms of each order in Θ separately yields a series of basic equations which will be used in the following:

$$H|n\rangle = E_n|n\rangle, \tag{2.8a}$$

$$(H - E_n)|{}^1n\rangle + ({}^1U - {}^1E_n)|n\rangle = 0, \tag{2.8b}$$

$$(H - E_n)|{}^2n\rangle + ({}^1U - {}^1E_n)|{}^1n\rangle + ({}^2U - {}^2E_n)|n\rangle = 0, \tag{2.8c}$$

$$\vdots$$

$$\sum_{j=0}^{N} ({}^jU - {}^jE_n)|{}^{N-j}n\rangle = 0, \tag{2.8d}$$

with $N = 0, 1, 2, \ldots$ and the obvious change of notation ${}^0U = H$ and $|{}^0n\rangle = |n\rangle$.

From the above set of basic equations all relevant quantities can be obtained. Using the Taylor expansion of the perturbation $\mathscr{U}$ the complex eigenenergy of the state n adopts the following form:

$$\begin{aligned}\mathscr{E}_n = E_n &+ \mathrm{i}\Theta\left[-2T_{nn} - i\left(\frac{\partial \mathscr{v}_{nn}}{\partial\Theta}\right)_{\Theta=0}\right] \\ &- \Theta^2\left[2T_{nn} - \tfrac{1}{2}\left(\frac{\partial^2 \mathscr{v}_{nn}}{\partial\Theta^2}\right)_{\Theta=0} - \langle {}^1n^*|H - E_n|{}^1n\rangle\right]. \end{aligned} \tag{2.9}$$

In order to determine the correction to the state $|n\rangle$ in first order it is convenient to write

$$|{}^1n\rangle = \sum_{a\neq n} |a\rangle C_{an}. \tag{2.10}$$

From Eq. (2.8b) follows immediately that

$$C_{an} = \frac{\langle a|2T + \mathrm{i}\left(\dfrac{\partial \mathscr{v}}{\partial\Theta}\right)_{\Theta=0}|n\rangle}{E_a - E_n}. \tag{2.11}$$

Analogously, the correction to $|n\rangle$ in second order is given by

$$|{}^2n\rangle = \sum_{a\neq n} |a\rangle \frac{\langle a|2T + \mathrm{i}\left(\dfrac{\partial \mathscr{v}}{\partial\Theta}\right)_{\Theta=0}|{}^1n\rangle + \langle a| - 2T + \tfrac{1}{2}\left(\dfrac{\partial^2 \mathscr{v}}{\partial\Theta^2}\right)_{\Theta=0}|n\rangle}{E_a - E_n}. \tag{2.12}$$

or, alternatively, as

$$|^2n\rangle = \sum_{a\neq n} \frac{|a\rangle}{E_a - E_n} \left\{ \left(-2T_{an} + \tfrac{1}{2}\left(\frac{\partial^2 v_{an}}{\partial\Theta^2}\right)_{\Theta=0} \right) + \sum_{b\neq n} \frac{\left[2T_{ab} + \mathrm{i}\left(\frac{\partial v_{ab}}{\partial\Theta}\right)_{\Theta=0}\right]\left[2T_{bn} + \mathrm{i}\left(\frac{\partial v_{bn}}{\partial\Theta}\right)_{\Theta=0}\right]}{E_b - E_n} \right\}. \tag{2.13}$$

From the energy formula (2.9) we derive two general stationarity conditions expressing the independence of $\mathscr{E}$ from the transformation parameter Θ. The first of these, ${}^1E_n = 0$, is nothing but the complex virial theorem

$$2T_{nn} = -\mathrm{i}\left(\frac{\partial v_{nn}}{\partial\Theta}\right)_{\Theta=0}, \tag{2.14}$$

while the other, ${}^2E_n = 0$, leads to

$$2T_{nn} = \tfrac{1}{2}\left(\frac{\partial^2 v_{nn}}{\partial\Theta^2}\right)_{\Theta=0} + \langle {}^1n^*|H - E_n|{}^1n\rangle. \tag{2.15}$$

which is a second order sum rule. Similarly, higher order sum rules can be derived in a straightforward manner.

3 The Dilated Coulomb Problem

3.1 *The general case*

In this case the expansion of the perturbation adopts the following simple form

$$\mathscr{U} = \mathrm{i}\Theta[-2T - V] - \Theta^2[2T + \tfrac{1}{2}V] + O(\Theta^3). \tag{3.1}$$

A further convenient simplification is

$$\frac{\langle n^*|\mathscr{U}|n\rangle}{\langle n^*|n\rangle} = \mathrm{i}\Theta[-T_{nn} - E_n] - \Theta^2[\tfrac{3}{2}T_{nn} + \tfrac{1}{2}E_n + \langle n|V|{}^1n\rangle + \langle {}^1n|V|n\rangle] + O(\Theta^3), \tag{3.2}$$

so that the energy expansion reads as

$$\mathscr{E}_n = E_n + \mathrm{i}\Theta[-T_{nn} - E_n] - \Theta^2[\tfrac{3}{2}T_{nn} + \tfrac{1}{2}E_n - \langle {}^1n^*|H - E_n|{}^1n\rangle] + O(\Theta^3). \tag{3.3}$$

The terms in square brackets, when equated to zero, yield the complex virial theorem and the sum rule in second order, respectively.

The first and second order sum rules above have been derived before for the Coulomb potential only and put to use for basis set optimization in resonance calculations [5, 8]. In such applications one does not expand about an undilated solution but regards as the unperturbed system one which is obtained at a finite value of the dilatation parameter, say Θ_0, and uses the parameter Θ as an additional, preferably small dilatation starting from Θ_0.

The sum rule in second order has a useful representation in terms of the eigenvalues of H and matrix elements of the kinetic energy operator alone:

$$E_n = -\sum_{a \neq n} \frac{T_{na}T_{an}}{E_a - E_n}. \tag{3.4}$$

Because the expansion of the perturbation is particularly simple for the Coulomb potential we include for this case also the sum rule in third order:

$$E_n = \tfrac{3}{2} \sum_{a \neq n} \sum_{b(\neq a,\, \neq n)} \frac{T_{na}V_{ab}T_{bn}}{(E_a - E_n)(E_b - E_n)}. \tag{3.5}$$

The first two corrections to the state vector are, respectively,

$$|{}^1n\rangle = -\sum_{a \neq n} \frac{|a\rangle V_{an}}{E_a - E_n}, \tag{3.6}$$

and

$$|{}^2n\rangle = \tfrac{3}{2} \sum_{a \neq n} \frac{|a\rangle V_{an}}{E_a - E_n} - \sum_{b \neq n} \sum_{a(\neq b,\, \neq n)} \frac{|b\rangle V_{ba}V_{an}}{(E_b - E_n)(E_a - E_n)}. \tag{3.7}$$

Of course, in these formulae the nondiagonal matrix elements of V may be replaced by the negative of the corresponding matrix elements of T. We notice especially that the first-order correction to both the energy and the state vector are purely imaginary (see Eqs. (2.4) and (2.9)) while the second-order corrections are both real. This alternating behavior continues to all orders.

3.2 Molecular fixed-nuclei case

In the preceding subsection we addressed the case where all the particles of the system interact via Coulomb forces and possess kinetic energy, especially atoms and molecules. The dilated Hamiltonian is obtained by replacing all position vectors $\boldsymbol{r}$ by $\boldsymbol{r}\exp(\mathrm{i}\Theta)$. For molecules the set of position vectors comprises those of the nuclei as well as those of the electrons. It is of particular interest to investigate the electronic energy of molecules as a function of the internuclear coordinates. The appropriate dilated Hamiltonian is obtained from the general form discussed above by omitting the kinetic energy operator of the nuclei. Clearly the resulting *fixed-nuclei Hamiltonian*

$$\mathscr{H} = H + \mathscr{U}, \tag{3.8a}$$

$$H = T + V, \tag{3.8b}$$

$$\mathscr{U} = T(e^{-2\mathrm{i}\Theta} - 1) + V(e^{-\mathrm{i}\Theta} - 1) \tag{3.8c}$$

is formally identical to that discussed in the preceding subsection. The quantity T is now the kinetic energy of the electrons and the potential V contains the electron–electron, electron–nucleus and the nucleus–nucleus Coulomb interactions and thus depends on the positions of the nuclei which will now be collectively symbolized by $\boldsymbol{R}$. For interesting previous work on the treatment of dilatation analyticity for nuclear coordinates in the framework of the Born–Oppenheimer approximation we refer to Refs. 15–17.

The Schrödinger equation for the dilated fixed-nuclei Hamiltonian reads

$$\mathcal{H}\,|\varkappa(\Theta, \boldsymbol{R}e^{\mathrm{i}\Theta})\rangle = \mathcal{E}_n(\Theta, \boldsymbol{R}e^{\mathrm{i}\Theta})\,|\varkappa(\Theta, \boldsymbol{R}e^{\mathrm{i}\Theta})\rangle, \tag{3.9}$$

where we have explicitly indicated that the electronic wave function and the electronic energy depend on Θ through the electronic coordinates as well as through the dilated nuclear coordinates. By writing

$$\boldsymbol{R}e^{\mathrm{i}\Theta} = \boldsymbol{R} + \boldsymbol{R}(e^{\mathrm{i}\Theta} - 1). \tag{3.10}$$

we may expand $|\varkappa\rangle$ and $\mathcal{E}_n$ about $\boldsymbol{R}$ to obtain

$$\begin{aligned}\mathcal{E}_n(\Theta, \boldsymbol{R}e^{\mathrm{i}\Theta}) &= \mathcal{E}_n(\Theta, \boldsymbol{R}) + (\nabla_{\boldsymbol{R}}\mathcal{E}_n(\Theta, \boldsymbol{R}))\cdot\boldsymbol{R}(e^{\mathrm{i}\Theta} - 1)\\ &\quad + \tfrac{1}{2}(\nabla_{\boldsymbol{R}}(\nabla_{\boldsymbol{R}}\mathcal{E}_n(\Theta, \boldsymbol{R}))\cdot\boldsymbol{R})\cdot\boldsymbol{R}(e^{\mathrm{i}\Theta} - 1)^2 + \cdots\end{aligned} \tag{3.11}$$

for the energy. An analogous equation holds for the dilated wavefunction.

Following our procedures in the preceding sections the energy function $\mathcal{E}_n(\Theta, \boldsymbol{R})$ may now be expanded about $\Theta = 0$ for bound states or about $\Theta = \Theta_0$ for resonances, with $\boldsymbol{R}$ just playing the role of an external parameter:

$$\mathcal{E}_n(\Theta, \boldsymbol{R}) = E_n(\boldsymbol{R}) + \mathrm{i}\Theta\,{}^1E_n(\boldsymbol{R}) - \Theta^2\,{}^2E_n(\boldsymbol{R}) + O(\Theta^3). \tag{3.12}$$

Inserting the expansions (3.11) and (3.12) and the corresponding ones for the wavefunction into the Schrödinger equation (3.9) and equating equal powers of Θ on both sides yields again a set of basic equations

$$H|n(\boldsymbol{R})\rangle = E_n(\boldsymbol{R})|n(\boldsymbol{R})\rangle, \tag{3.13a}$$

$$\{{}^1U - [{}^1E_n + (\nabla_{\boldsymbol{R}}E_n)\cdot\boldsymbol{R}]\}|n\rangle + (H - E_n)|{}^1n\rangle = 0, \tag{3.13b}$$

and

$$\begin{aligned}&\{{}^2U - [{}^2E_n + \tfrac{1}{2}(\nabla_{\boldsymbol{R}}E_n)\cdot\boldsymbol{R} + (\nabla_{\boldsymbol{R}}{}^1E_n)\cdot\boldsymbol{R} + \tfrac{1}{2}(\nabla_{\boldsymbol{R}}(\nabla_{\boldsymbol{R}}E_n)\cdot\boldsymbol{R})\cdot\boldsymbol{R}]\}|n\rangle\\ &\quad + \{{}^1U - [{}^1E_n + (\nabla_{\boldsymbol{R}}E_n)\cdot\boldsymbol{R}]\}|{}^1n\rangle + (H - E_n)|{}^2n\rangle = 0,\end{aligned} \tag{3.13c}$$

where $|{}^1n\rangle$, $|{}^2n\rangle$ ... are defined as the coefficients in the expansion of $|\varkappa(\Theta, \boldsymbol{R}e^{\mathrm{i}\Theta})\rangle$ in powers of $\mathrm{i}\Theta$.

Multiplying Eq. (3.13b) by $\langle n|$ and making use of the fact that the energies $\mathcal{E}_n(\Theta, \boldsymbol{R})$ should be independent of Θ, i.e. ${}^1E_n = {}^2E_n = \cdots = 0$, we readily obtain

$$E_n(\boldsymbol{R}) + T_{nn} + (\nabla_{\boldsymbol{R}}E_n(\boldsymbol{R}))\cdot\boldsymbol{R} = 0, \tag{3.14}$$

which is the well known virial theorem for fixed-nuclei molecules. At the molecular equilibrium geometry $\nabla_{\boldsymbol{R}}E_n(\boldsymbol{R})$ vanishes and Eq. (3.14) reduces to $E_n + T_{nn} = 0$, the same expression as for atoms.

As before we write

$$|{}^1n(\boldsymbol{R})\rangle = \sum_{a \neq n} C_{an}(\boldsymbol{R})|a(\boldsymbol{R})\rangle, \tag{3.15a}$$

with the coefficients obtained from Eq. (3.13b) as

$$C_{an} = \frac{T_{an}}{E_a - E_n}. \tag{3.15b}$$

Inserting this result into the basic equation (3.13c) yields, after multiplication by

$\langle n|$, the new sum rule in second order

$$E_n(\boldsymbol{R}) + 2T_{nn} = \sum_{a \neq n} \frac{|T_{an}|^2}{E_a - E_n} + \tfrac{1}{2}(\nabla_{\boldsymbol{R}}(\nabla_{\boldsymbol{R}} E_n)\cdot\boldsymbol{R})\cdot\boldsymbol{R}, \tag{3.16}$$

which should be compared to Eq. (3.4) for atoms. The last term on the r.h.s. of Eq. (3.16) does not vanish, not even at the equilibrium geometry of the molecule.

Denoting the coordinate of the kth nucleus by $\boldsymbol{R}_k$, the collective coordinate is given by $\boldsymbol{R} = (\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_M)$ and one finds

$$(\nabla_{\boldsymbol{R}} E_n)\cdot\boldsymbol{R} = \sum_{k=1}^{M} \frac{\partial E_n}{\partial \boldsymbol{R}_k}\cdot\boldsymbol{R}_k, \tag{3.17}$$

$$(\nabla_{\boldsymbol{R}}(\nabla_{\boldsymbol{R}} E_n)\cdot\boldsymbol{R})\cdot\boldsymbol{R} = \sum_{k,k'=1}^{M} \boldsymbol{R}_{k'}\cdot\frac{\partial^2 E_n}{\partial \boldsymbol{R}_{k'}\partial \boldsymbol{R}_k}\cdot\boldsymbol{R}_k. \tag{3.18}$$

For diatomic molecules, in particular, the virial theorem and the sum rule in second order take on the very simple forms:

$$E_n + T_{nn} + R\frac{\partial E_n}{\partial R} = 0, \tag{3.19}$$

$$E_n + 2T_{nn} = \sum_{a \neq n} \frac{|T_{an}|^2}{E_a - E_n} + \tfrac{1}{2}R^2\frac{\partial^2 E_n}{\partial R^2}, \tag{3.20}$$

where R is the *internuclear distance.*

4 Dilated Hartree–Fock Theory with Coulomb Forces

In order to calculate the effect of dilatation transformations on orbitals and orbital energies we start from the Fock operator $F = t + V$ where the potential V is defined as

$$V = v + \sum_{j=1}^{N} \langle j||j\rangle, \tag{4.1}$$

with the single particle kinetic energy operator $t = -\frac{1}{2}\nabla^2$ and the electron–nucleus potential $v = -Z/r$. For simplicity we confine this discussion to atoms but emphasize that molecules can be treated analogously by following the approach discussed in section 3.2. We make also use of the usual two-particle operator definition

$$\langle f||g\rangle h \equiv \int d^3y f^*(y)\frac{1}{|\boldsymbol{x} - \boldsymbol{y}|}[g(y)h(x) - h(y)g(x)], \tag{4.2}$$

which can be turned into an antisymmetrized two-electron repulsion integral $\langle jf||gh\rangle$ by multiplication by $j^*(x)h(x)$ and subsequent integration over the range of the variable $\boldsymbol{x}$.

The orbital equation is

$$F|m\rangle = \varepsilon_m|m\rangle, \tag{4.3}$$

with its dilated version

$$\mathscr{F}|\mathscr{m}\rangle = \mathscr{E}_m|\mathscr{m}\rangle, \tag{4.4}$$

where the following definition of $\mathscr{F}$ is understood

$$\mathscr{F} = te^{-2\mathrm{i}\Theta} + \left[v + \sum_{j=1}^{N} \langle \mathscr{j}^* || \mathscr{j} \rangle \right] e^{-\mathrm{i}\Theta}. \tag{4.5}$$

Following the notation of Eq. (1.2) we rewrite this operator as

$$\mathscr{F} = F + [(e^{-2\mathrm{i}\Theta} - 1)t + (\mathscr{v} - V)], \tag{4.6}$$

with

$$\mathscr{v} = e^{-\mathrm{i}\Theta}\left[v + \sum_{j=1}^{N} \langle \mathscr{j}^* || \mathscr{j} \rangle \right]. \tag{4.7}$$

The expansion of $\mathscr{F}$ in powers of $\mathrm{i}\Theta$ is given by

$$\mathscr{F} = F + {}^1F\mathrm{i}\Theta - {}^2F\Theta^2 + \cdots, \tag{4.8}$$

with

$${}^1F = -(F + t) + \sum_{j=1}^{N} [\langle {}^1j^* || j \rangle + \langle j || {}^1j \rangle] \tag{4.9}$$

and

$$\begin{aligned} {}^2F = \tfrac{1}{2}(F + 3t) + \sum_{j=1}^{N} [&\langle {}^1j^* || {}^1j \rangle - \langle {}^1j^* || j \rangle \\ &- \langle j || {}^1j \rangle + \langle {}^2j^* || j \rangle + \langle j || {}^2j \rangle - \langle j || j \rangle \langle {}^1j^* | {}^1j \rangle]. \end{aligned} \tag{4.10}$$

Using these definitions we rewrite Eq. (4.4) as

$$\begin{aligned} &(F + {}^1F\mathrm{i}\Theta - {}^2F\Theta^2 + \cdots)|j + {}^1j\mathrm{i}\Theta - {}^2j\Theta^2 + \cdots\rangle \\ &\quad = (\varepsilon_j + {}^1\varepsilon_j\mathrm{i}\Theta - {}^2\varepsilon_j\Theta^2 + \cdots)|j + {}^1j\mathrm{i}\Theta - {}^2j\Theta^2 + \cdots\rangle. \end{aligned} \tag{4.11}$$

Equating terms of equal power in Θ yields the following chain of equations:

$$(F - \varepsilon_j)|j\rangle = 0, \tag{4.12}$$

$$(F - \varepsilon_j)|{}^1j\rangle = ({}^1\varepsilon_j - {}^1F)|j\rangle, \tag{4.13}$$

$$(F - \varepsilon_j)|{}^2j\rangle = ({}^1\varepsilon_j - {}^1F)|{}^1j\rangle + ({}^2\varepsilon_j - {}^2F)|j\rangle, \tag{4.14}$$

from which the corrections in first and second order are obtained.

We notice from Eq. (4.13) that

$$|{}^1n\rangle = \sum_{\nu \neq n} |\nu\rangle \frac{\langle \nu | {}^1\varepsilon_n - {}^1F | n \rangle}{\varepsilon_\nu - \varepsilon_n} \equiv \sum_{\nu \neq n} |\nu\rangle C_{\nu n}. \tag{4.15}$$

This equation defines a set of coefficients $C_{\nu n}$ which will be calculated later. The orbital energy correction in first order is

$${}^1\varepsilon_n = \langle n | {}^1F | n \rangle. \tag{4.16}$$

Using Eqs. (4.9) and (4.15) this may be rewritten as

$${}^1\varepsilon_n = -(\varepsilon_n + t_{nn}) + 2 \sum_{j=1}^{N} \sum_{\nu \neq j} \langle jn || \nu n \rangle C_{\nu j}. \tag{4.17}$$

From the first order equation (4.13) we obtain upon multigration by $\langle \mu |$ the following system of inhomogeneous linear equations for the determination of the coefficients $C_{\nu j}$:

$$\sum_{j=1}^{N} \sum_{\nu \neq j} [(\varepsilon_\nu - \varepsilon_j)\delta_{\mu\nu}\delta_{nj} + \langle j\mu || \nu n\rangle + \langle \nu\mu || jn\rangle] C_{\nu j} = t_{\mu n}, \tag{4.18}$$

which is valid for $\mu \neq n$. Equations similar to Eq. (4.18); i.e. coupled HF equations, have been used by Dalgarno in polarizability calculations [18]. For further original work on the coupled HF equations, see also Refs. 19–21.

In a similar fashion we derive from Eq. (4.14) the following expression in second order

$${}^2\varepsilon_n = \langle n|{}^1F|{}^1n\rangle + \langle n|{}^2F|n\rangle, \tag{4.19}$$

which can be rewritten as

$$\begin{aligned} {}^2\varepsilon_n = {} & \tfrac{1}{2}\varepsilon_n + \tfrac{3}{2}t_{nn} - \langle n|t|{}^1n\rangle + \sum_{j=1}^{N} [\langle {}^1j^*n||{}^1jn\rangle + \langle {}^1j^*n||j{}^1n\rangle \\ & + \langle jn||{}^1j{}^1n\rangle - \langle {}^1j^*n||jn\rangle - \langle jn||{}^1jn\rangle + \langle {}^2j^*n||jn\rangle + \langle jn||{}^2jn\rangle \\ & - \langle jn||jn\rangle\langle {}^1j^*|{}^1j\rangle]. \end{aligned} \tag{4.20}$$

In analogy to Eq. (4.15) we introduce a set of coefficients $D_{\nu n}$ in second order by

$$|{}^2n\rangle = \sum_{\nu \neq n} |\nu\rangle D_{\nu n}.$$

The system of equations for the calculation of the coefficients $D_{\nu n}$ is then given by

$$\sum_{j=1}^{N} \sum_{\nu \neq j} [(\varepsilon_\nu - \varepsilon_j)\delta_{\mu\nu}\delta_{nj} + \langle j\mu || \nu n\rangle + \langle \nu\mu || jn\rangle] D_{\nu j} = K_{\mu n}, \tag{4.21}$$

which is valid for $\mu \neq n$. The driving term $K_{\mu n}$ is known once all relevant quantities of first order are known:

$$\begin{aligned} K_{\mu n} = {} & -\frac{5}{2} t_{\mu n} + \langle \mu | {}^1\varepsilon_n + 2\varepsilon_\mu - \varepsilon_n + t | {}^1n\rangle \\ & - \sum_{j=1}^{N} [\langle {}^1j^*\mu || j{}^1n\rangle + \langle j\mu || {}^1j{}^1n\rangle \\ & + \langle {}^1j^*\mu || {}^1jn\rangle - \langle j\mu || jn\rangle\langle {}^1j^*|{}^1j\rangle]. \end{aligned} \tag{4.22}$$

We notice, in particular, that the corrections of the orbital energies in nth order depend on the corrections to the orbitals of the same order. This is caused by the dependence of the Fock operator on the orbitals. As soon as we combine these results to obtain the total HF energy the dependence on the same order corrections drops out. Let $\mathscr{D}$ designate the dilated Slater determinant. Then the dilated HF energy functional reads as

$$\mathscr{E}^{\mathrm{HF}} = \frac{\langle \mathscr{D}^* | \mathscr{H} | \mathscr{D}\rangle}{\langle \mathscr{D}^* | \mathscr{D}\rangle}. \tag{4.23}$$

The expansion of the HF energy is given by

$$\begin{aligned}\mathscr{E}^{\mathrm{HF}} &= E^{\mathrm{HF}} + \mathrm{i}\Theta\, {}^{1}E^{\mathrm{HF}} - \Theta^{2}\, {}^{2}E^{\mathrm{HF}} + \cdots \\ &= \sum_{n=1}^{N} \Bigg[(\varepsilon_n + \mathrm{i}\Theta\, {}^{1}\varepsilon_n - \Theta^{2}\, {}^{2}\varepsilon_n + \cdots) \\ &\qquad - \tfrac{1}{2}(1 - \mathrm{i}\Theta - \tfrac{1}{2}\Theta^{2} + \cdots) \sum_{j=1}^{N} \langle \mathscr{j}^{*}\mathscr{n}^{*} || \mathscr{j}\mathscr{n} \rangle \Bigg]. \end{aligned} \tag{4.24}$$

Note that the dilated orbitals $\mathscr{j}$ and $\mathscr{n}$ in this equation are normalized.

Lengthy but straightforward evaluation of the individual orders yields

$$ {}^{1}E^{\mathrm{HF}} = -(E^{\mathrm{HF}} + T^{\mathrm{HF}}), \tag{4.25}$$

$$ {}^{2}E^{\mathrm{HF}} = -(E^{\mathrm{HF}} + \langle D | T | {}^{1}D \rangle), \tag{4.26}$$

where T^{HF} is the usual Hartree–Fock kinetic energy and D the HF Slater determinant.

Let us briefly comment on the above results. Because of

$$\begin{aligned} 0 &= \langle \mathscr{a}^{*} | \mathscr{n} \rangle \\ &= \mathrm{i}\Theta[\langle {}^{1}a^{*} | n \rangle + \langle a | {}^{1}n \rangle] - \Theta^{2}[\langle {}^{2}a^{*} | n \rangle + \langle a | {}^{2}n \rangle + \langle {}^{1}a^{*} | {}^{1}n \rangle] + \cdots \end{aligned} \tag{4.27a}$$

for $a \neq n$, we find readily that

$$ C_{an} = -C_{na}, \tag{4.27b}$$

$$ D_{an} = -D_{na} - \sum_{\nu} C_{\nu a} C_{\nu n}. \tag{4.27c}$$

Consequently, Eq. (4.18) can be rewritten for $\mu > N$, $n \leqslant N$ to give

$$\sum_{j=1}^{N} \sum_{\nu=N+1}^{\infty} [(\varepsilon_\nu - \varepsilon_j)\delta_{\mu\nu}\delta_{nj} + \langle j\mu || \nu n \rangle + \langle \nu\mu || jn \rangle] C_{\nu j} = t_{\mu n}. \tag{4.28}$$

In Eq. (4.21), a similar restriction on the summation index ν results if the driving term $K_{\mu n}$ is slightly modified.

Introducing the vectors $\boldsymbol{t}$ and $\boldsymbol{C}$ with elements t_p and C_p, where p runs over the pairs μn with $\mu > N$ and $n \leqslant N$, we may use Eq. (4.28) to write

$$\boldsymbol{C} = \boldsymbol{S}^{-1}\boldsymbol{t}. \tag{4.29a}$$

Here, $\boldsymbol{S}$ is the Thouless instability matrix [22] with elements

$$S_{pq} = (\varepsilon_\nu - \varepsilon_j)\delta_{\mu\nu}\delta_{nj} + \langle j\mu || \nu n \rangle + \langle \nu\mu || jn \rangle, \tag{4.29b}$$

where $p = \{\mu n;\ \mu > N,\ n \leqslant N\}$ and $q = \{\nu j;\ \nu > N,\ j \leqslant N\}$.

Equation (4.26) can now be expressed in terms of matrix elements of the one-particle kinetic energy operator t and the universal Thouless instability matrix

$$-{}^{2}E^{\mathrm{HF}} = E^{\mathrm{HF}} + \boldsymbol{t}^{+}\boldsymbol{S}^{-1}\boldsymbol{t}. \tag{4.30}$$

This expression may be compared to the corresponding one for the exact, i.e. not HF, energy. This equation reads as

$$-{}^{2}E_{0} = E_{0} + \boldsymbol{T}^{+}\boldsymbol{\Delta}^{-1}\boldsymbol{T} \tag{4.31}$$

where $\boldsymbol{T}$ is a vector with elements T_{0n}, $n \neq 0$, and Δ is the diagonal matrix of the energy differences $E_n - E_0$. It should be noted that, while Δ is a positive definite matrix for systems with a non-degenerate ground state, the Thouless instability matrix can, in principle, have vanishing or even negative eigenvalues (see references given in Ref. [14]).

5 Conclusion

In this work energies and states of dilated Hamiltonians have been expressed as an expansion in powers of the dilatation parameter Θ. One of the fundamental properties of dilatation analytic potentials is that their spectrum may contain complex eigenvalues which are independent from the dilatation parameter once they are "uncovered" in a simple geometric visualization with the Θ-dependent continuum cut(s) fanning into the lower half of the complex plane. This Θ independence of the eigenvalues, which, as a special case, holds also for the energies of bound states, has been used to derive sum rules. The theory has been presented for general dilatation analytic potentials and is then extended to potentials depending on external parameters which are affected by the dilatation (e.g. nuclear coordinates in molecules), as well as to self-consistent potentials.

For atoms, for instance, the energy expansion reads (see section 3)

$$\begin{aligned}\mathscr{E}_n(\Theta) = E_n - \mathrm{i}\Theta[T_{nn} + E_n] - \Theta^2[\tfrac{3}{2}T_{nn} + \tfrac{1}{2}E_n \\ - \sum_{a \neq n} T_{na}(E_a - E_n)^{-1}T_{an}] + \cdots .\end{aligned} \tag{5.1}$$

The independence of $\mathscr{E}_n$ from Θ gives rise to infinitely many exact sum rules of increasing order. On the other hand, the sum rules may not be exactly satisfied in practical computations. Then the expansion can still be useful in analyzing the resulting dependence from Θ. It is expected that, as the order of the sum rule increases, approximations and numerical inaccuracies will be more noticeable and the sum rules become harder to satisfy. For the electronic ground state $n = 0$, as an example, an approximate variational calculation as they are customarily done may quite accurately predict the energy and even satisfy the virial theorem. It is, however, possible and even likely that the sum rule of second order is grossly violated because it describes the balance between a ground state quantity, $\frac{3}{2}T_{00} + \frac{1}{2}E_0$, and a term which is related to all excited states, $\sum_{a \neq 0} T_{0a}(E_a - E_0)^{-1}$ T_{a0}. Consequently, the computed complex energy will depend on Θ unless all sum rules are enforced.

A similar expansion holds for the total Hartree–Fock energy (see Sect. 4),

$$\mathscr{E}^{\mathrm{HF}}(\Theta) = E^{\mathrm{HF}} - \mathrm{i}\Theta[T^{\mathrm{HF}} + E^{\mathrm{HF}}] + \Theta^2[E^{\mathrm{HF}} + \boldsymbol{t}^+\boldsymbol{S}^{-1}\boldsymbol{t}] + \cdots . \tag{5.2}$$

If, for a bound state, the virial theorem is not accurately satisfied due to numerical errors, the computed energy will exhibit an imaginary part which is linear in Θ for small Θ. Analogous results hold for a resonance state. Using finite basis sets in quantum calculations with complex rotation leads to a Θ dependence of the results which can become quite severe as is indicated by expansion (5.2). In the second order sum rule, for example, E^{HF} contains only properties of the occupied orbitals while its compensating term $\boldsymbol{t}^+\boldsymbol{S}^{-1}\boldsymbol{t}$ depends strongly on the virtual orbitals which, in turn, are sensitive to the choice of the basis set. Our discussion above makes clear that sum rules should be utilized in practical computations of resonances as emphasized earlier [8]. We mention briefly that even the fully numerical complex Hartree–Fock calculation of Bentley [23] for a system as simple as the ground state of the beryllium atom exhibits some dependence on Θ (imaginary as well as real) which, assuming that no systematic Θ dependence is present, can be traced back to errors on the real axis following essentially the expansion above.

Here, we would like to touch upon a point of general relevance for self-consistent potentials. It has been recently argued [14] that such total and one-particle potentials may not be dilatational analytic and the corresponding energy eigenvalues may thus depend on Θ in an essential manner (i.e. not resulting from rounding errors). The range of the non-analyticity and, in particular, the strength of its impact on the energies may vary substantially. The non-analyticity effects are expected to be smallest for few-electron closed-shell atoms like helium and larger for many-electron open-shell atoms and, in particular, open-shell molecules [14]. For the helium atom, as an example, only s-orbitals are occupied. Consequently, the Thouless instability matrix $\boldsymbol{S}$ exhibits only large positive eigenvalues and the response of the system to changes in Θ is likely to be correspondingly small. Even in the case of negligible non-analyticity effects the Θ-expansion provides, in many situations, valuable information for parameter optimization and, in most cases, handy tools for the quality assessment of a particular calculation [8].

As mentioned above, the main goal of the present work is the derivation of exact sum rules for general potentials including self-consistent field potentials. Being exact relations, the sum rules are interesting by themselves. We mention briefly that such sum rules been used successfully in previous practical calculations [5, 8] of resonances for a few specific potentials. Their usefulness for the optimization of bound state calculations has not yet been demonstrated explicitly. For this problem, however, alternative optimization procedures are known. The sum rules have been derived via a perturbation expansion in powers of $(\Theta - \Theta_0)$, where Θ_0 is the exact dilatation angle of the resonance ($\Theta_0 = 0$ for bound states; for simplicity of notation the difference $\Theta - \Theta_0$ is usually referred to just as Θ in the text). In principle, one may also apply an analogous perturbation expansion about some unperturbed Hamiltonian in order to directly compute resonances. Starting from an unperturbed hermitian (i.e. unrotated) Hamiltonian and taking essentially $[e^{i\Theta} - 1]$ as the perturbational parameter, Moiseyev and Certain [24] have shown that for resonances of helium the radius of convergence of the perturbation series is painfully small. Although their expansion is different from ours, we can infer from our experience that the direct use of the perturbation series in the calculation of resonances is not recommendable unless a suitable unperturbed Hamiltonian is initially known (e.g. if Θ_0 is approximately known).

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