Time evolution and non-Hermiticity in quantum defect theory

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Abstract
Quantum defect theory (QDT) is widely employed to describe Rydberg states.
We show that the effective Hamiltonian employed by QDT is intrinsically
non-Hermitian and examine the consequences arising in practical calculations.
In particular if the eigenstates are treated in the 'standard' manner, i.e. as if
the Hamiltonian were Hermitian, unphysical errors may appear, such as the
non-unitarity of the time evolution. Although in most cases the degree of non-
Hermiticity is small, we give examples involving the autocorrelation function
and the time dependence of entanglement generation where non-Hermiticity
must be explicitly accounted for to avoid such unphysical errors. This is done by
introducing a second basis set forming with the QDT eigenstates a biorthogonal
basis. We give practical schemes to construct this basis and discuss how to
express physical quantities. We illustrate the formalism by computing the
time evolution of the autocorrelation function and of the linear entropy for a
model Rydberg system and compare with the results obtained in the 'standard'
manner.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The axioms of quantum mechanics require physical observables of a closed system to be
represented by Hermitian operators acting on a Hilbert space. The Hamiltonian is generally
the most important operator: it determines the energy eigenstates of the system, from which
probabilities and expectation values are computed. As is well known, open systems are
modelled with complex potentials, thus yielding a non-Hermitian Hamiltonian with complex
eigenvalues; non-Hermiticity then gives rise to specific problems, in particular for determining
the time evolution [1, 2]. Less well known is the case of real Hamiltonians that are nevertheless
non-Hermitian. However Bloch [3] pointed out long ago that the scattering formalism
describing nuclear reactions was non-Hermitian when limited to the reaction zone. This fact is

routinely employed by practitioners of R-matrix theory [4] when computing electron-scattering processes in atomic and molecular physics.

Quantum defect theory [5, 6] (QDT, or MQDT for multichannel QDT) is precisely concerned by the scattering of an electron (the 'Rydberg' electron) on an atomic or molecular ion core. It is the main theoretical tool employed to describe the discrete and continuum spectra of excited atomic and molecular Rydberg states. The complex spectral patterns are explained as the result of interchannel couplings resulting from the collision between the outer electron and the ionic core. The power of QDT lies in the use of a scattering-theory based formalism that explicitly includes closed channels to account for the bound states of the system. The eigenstates of the system are obtained in terms of the collision channel functions, which are only defined *outside* the collision region. In this outer region, the Hamiltonian is non-Hermitian. Although non-Hermiticity does not affect the validity of the energies and eigenfunctions given by QDT, the standard *expansions* of wavefunctions and operators on the eigenstates of the Hamiltonian are not strictly valid. This may in principle induce errors when computing certain quantities, such as the time evolution operator. The knowledge of the evolution operator is crucial in the determination of Rydberg wave packet dynamics, which has become an important tool in the understanding of time-dependent phenomena such as the implementation of coherent control [7].

We investigate in this work the non-Hermitian aspects of quantum defect theory. To the best of our knowledge, the study of these aspects seems to have been neglected, despite the popularity of QDT. Indeed in most practical cases non-Hermiticity is small and can rightly be neglected when working with operator expansions. Notwithstanding we will put forward examples for which ignoring non-Hermiticity can bring in noticeable numerical errors. We will first give an overview of the scattering formalism of quantum defect theory (section 2). This will allow us to pinpoint in section 3 what is non-Hermitian in QDT and why this is so. Section 4 will be concerned by the introduction of a biorthogonal basis set and its associated metric, which are the elements we introduce to cope with non-Hermiticity. A way to implement practical calculations will be presented. We will then illustrate (section 5) the effects of non-Hermiticity in the time dependence of the autocorrelation function for Rydberg wave packets; a second illustration will deal with the time generation of entanglement as measured by the linear entropy associated with the reduced density matrix of the Rydberg electron. Further comments—in particular assessing when non-Hermitian issues should be taken into account in practical calculations—and our conclusions will be given in section 6.

2. Quantum defect theory

We give here a brief description of QDT. We will put the emphasis on the features that will be important in discussing non-Hermiticity below, so the presentation and notation might appear somewhat unorthodox relative to the standard approaches [5, 6]. In particular we shall mainly be concerned with bound states, since, as will be explained below, open channels are immune to the problems regarding Hermiticity. We shall also obliviate the important topic of frame transformations between different coupling regimes, since frame transformations will play no role in our subsequent discussions.

Let H^e be the total (exact) Hamiltonian of the Rydberg problem. The essence of QDT is to separate the total Hamiltonian H^e in two parts,

$$H^e = H_0 + V. \tag{1}$$

H_0 describes the dynamics of the Rydberg electron in the region outside the core. It is assumed to be exact in the outer region, where we have an effective 2-particle problem (the

outer electron and the core), and therefore contains the long range interactions between the outer electron and the core,

$$H_0 = \frac{p_r^2}{2m} + V_{\text{LR}}(r) + H_0^{\text{core}}. \tag{2}$$

V_{LR} represents the spherically symmetric long-range potential (in what follows, the Coulomb and centrifugal terms) and H_0^{core} is the 'free' Hamiltonian of the ionic core. The potential V describes the short range many-particle interactions, which are assumed to vanish outside the core,

$$V(r', r) = \theta(r_0 - r')V\theta(r_0 - r), \tag{3}$$

where θ is the step function and r_0 the effective radius of the core.

The eigenstates of H_0 are given by

$$|\phi_i(E)\rangle = |f_i(\epsilon_i)\rangle |i(E_i^+)\rangle. \tag{4}$$

E (a positive or negative real number) is the total energy of the system partitioned between the core energy E_i^+ (which is assumed to lie within the bound spectrum) and the outer electron energy ϵ_i:

$$E = E_i^+ + \epsilon_i. \tag{5}$$

$|i(E_i^+)\rangle$ is a compound notation accounting for the quantum state and the coupling of the angular momenta of the core and of the outer electron. The radial degree of freedom of the outer electron (r coordinate) is represented by $|f_i(\epsilon_i)\rangle$, a radial function regular at the origin. Note that if i is a bound channel, $f_i(r)$ diverges as $r \to \infty$ except when the energy is an eigenvalue of H_0.

When the short-range potential V is turned on, the channel solutions are obtained from the appropriately modified [8–10] Lippmann–Schwinger equations of scattering theory as

$$|\psi_i^e(E)\rangle = |\phi_i(E)\rangle + G_0(E)K(E)|\phi_i(E)\rangle, \tag{6}$$

where $G_0(E)$ is the standing wave Green's function and K the reaction (scattering) operator. If i is a bound channel $\langle r|\psi_i^e(E)\rangle$ generally always diverges radially. The eigenstates are obtained by the superposition

$$|\psi^e(E)\rangle = \sum_i Z_i(E)|\psi_i^e(E)\rangle. \tag{7}$$

The expansion coefficients $Z_i(E)$ are determined by the asymptotic ($r \to \infty$) boundary conditions. When all the channels are closed (which in this work is the case we shall be most interested in) this formal expression has a sense only if E is an eigenvalue of H^e

$$H^e|\psi^e(E)\rangle = E|\psi^e(E)\rangle \tag{8}$$

(otherwise this expression diverges as $r \to \infty$); we then put $\epsilon_i = -1/(2\nu_i^2)$. As required by quantum mechanics, the eigenstates are orthonormal

$$\langle \psi^e(E_1)|\psi^e(E_2)\rangle = \delta_{E_1 E_2} \tag{9}$$

whereas H^e is Hermitian and admits the spectral decomposition

$$H^e = \sum_E |\psi^e(E)\rangle\langle\psi^e(E)|E + \int_0^\infty dE|\psi^e(E)\rangle\langle\psi^e(E)|E, \tag{10}$$

where the discrete sum runs on the bound eigenvalues. Asymptotic completeness imposes orthogonality of the bound and continuum eigenstates of H^e.

Quantum defect theory enters by reducing the Green's function in equation (6) in order to obtain a tractable expression in terms of a radial solution $g(r)$ of H_0 irregular at the origin. However this reduction is only valid for $r > r_0$ where V vanishes. Equations (6) and (7) then become respectively [8–10]

$$\langle r | \psi_i(E) \rangle = f_i(\epsilon_i; r) | i \rangle - \sum_j g_j(\epsilon_i; r) K_{ji} | j \rangle \qquad r > r_0 \tag{11}$$

and

$$\langle r | \psi(E) \rangle = \sum_i B_i(E) | i \rangle F_i(\epsilon_i, r) \qquad r > r_0. \tag{12}$$

K_{ji} are the elements of the symmetric K matrix and F_i is a radial function defined by

$$F_i(\epsilon_i, r) = \cos \beta_i f_i(\epsilon_i; r) - \sin \beta_i g_i(\epsilon_i; r), \tag{13}$$

which goes to 0 as $r \longrightarrow \infty$. The phase β is given by $\beta_i = \pi(\nu_i - l_i)$ for closed channels and the coefficients B_i are readily obtained from the Z coefficients and the K matrix. We renormalize the channel functions $F_i(\epsilon_i, r)$ to unity, $\langle F_i(\epsilon_i) | F_i(\epsilon_i) \rangle = 1$ and therefore the coefficients B_i also contain the energy-normalization factors. Normalization of the eigenstates leads to

$$\sum_i |B_i(E)|^2 = 1. \tag{14}$$

Note that equation (12) is *exact* for $r > r_0$ but is not valid in the region $r < r_0$. Therefore it does not represent the eigenstate of the exact Hamiltonian, and this is why we have taken away the superscript e. However we can always write

$$|\psi^e(E)\rangle = \theta(r - r_0) |\psi(E)\rangle + \theta(r_0 - r) |\psi_{\text{inner}}(E)\rangle, \tag{15}$$

where the second term represents the eigenstate of H^e when the 'outer' electron enters the inner zone (so that as a matter of fact there is no more effective outer electron). Most importantly, E is the eigenvalue of H^e, but it is actually obtained from the sole QDT outer solutions provided the boundary conditions at r_0 are known. Indeed, the power of QDT is that it bypasses the knowledge of $|\psi_{\text{inner}}(E)\rangle$: only its knowledge on the boundary surface r_0 is necessary. This is consistent with the physical picture of having a Rydberg electron spending most of the time roaming far from the inner zone. Therefore it comes as no surprise that the scattering solutions are employed in many respects as if the inner wavefunction was irrelevant: for example, normalization does not depend on the details of $|\psi_{\text{inner}}(E)\rangle$, and we have

$$\langle \psi^e(E_1) | \psi^e(E_1) \rangle = \langle \psi(E_1) | \psi(E_1) \rangle = 1, \tag{16}$$

where the radial scalar product in the second term is only taken on the interval $[r_0, \infty]$. However, contrarily to the exact eigenstates, the restriction of the exact eigenstates to the outer zone spoils orthogonality, as discussed in the next section.

3. Quantum defect theory is non-Hermitian

3.1. What is non-Hermitian?

The exact Hamiltonian H^e encompasses both the inner and outer zones. However, quantum defect theory is only concerned by the outer region. The part of H^e in the outer region is

$$H \equiv \theta(r' - r_0) H^e \theta(r - r_0) \tag{17}$$

$$= \sum_E E |\psi(E)\rangle \langle \psi(E)|. \tag{18}$$

Although H is Hermitian and equation (18) looks like a spectral decomposition, it is easily established by using equation (15) that

$$H|\psi(E)\rangle = E|\psi(E)\rangle - \theta(r - r_0)H^e|\psi_{\text{inner}}(E)\rangle \tag{19}$$

$$\neq E|\psi(E)\rangle. \tag{20}$$

The last equation does not hold because of the boundary terms at $r = r_0$. Therefore the QDT functions $|\psi(E)\rangle$ are not eigenstates of H. It is also straightforward to see that they are not orthogonal, given that

$$\langle\psi(E)|\psi(E')\rangle = \sum_i B_i(E)B_i(E')\langle F_i(\epsilon_i)|F_i(\epsilon_i')\rangle. \tag{21}$$

The radial overlap integral $\langle F_i(\epsilon_i)|F_i(\epsilon_i')\rangle$ is unity if $\epsilon_i = \epsilon_i'$ and oscillates as a function of $\epsilon_i - \epsilon_i'$ for $\epsilon_i \neq \epsilon_i'$. For large values of ν_i and ν_i' the radial overlap can be calculated analytically as [11] (see also appendix A)

$$\langle F_i(\epsilon_i)|F_i(\epsilon_i')\rangle = \frac{\sin \pi(\nu_i' - \nu_i)}{\pi(\nu_i' - \nu_i)}. \tag{22}$$

Equations (20) and (21) have far-reaching consequences. For example if $\exp(-iHt)$ is employed as the time evolution operator, time evolution would become non-unitary and probability would not be conserved, since

$$\langle\psi(E)|\psi(E')\rangle \neq (\langle\psi(E)|e^{iHt})(e^{-iHt}|\psi(E')\rangle). \tag{23}$$

Note also that the average values of H are not the same as the exact averages obtained with H^e: if the system is in an exact state

$$|\chi^e\rangle = \sum_k \alpha_k|\psi^e(E_k)\rangle, \tag{24}$$

the outer states are given by

$$|\chi\rangle \equiv \theta(r - r_0)|\chi^e\rangle = \sum_k \alpha_k|\psi(E_k)\rangle. \tag{25}$$

We then have

$$\langle H^e\rangle_{\chi^e} = \sum_k |\alpha_k|^2 E_k \tag{26}$$

but

$$\langle H\rangle_\chi = \sum_{kk'n} E_n \alpha_{k'}^* \alpha_k \langle\psi(E_{k'})|\psi(E_n)\rangle\langle\psi(E_n)|\psi(E_k)\rangle. \tag{27}$$

The origin of these problems is that the QDT solutions are not eigenfunctions of H but of a non-Hermitian Hamiltonian $\widetilde{H}$. From equations (1) and (3) we see that $\widetilde{H}$ is formally given by H_0, but supplemented with two conditions. First $\widetilde{H}$ is only defined radially on $[r_0, +\infty]$ (just like H) whereas H_0 and H^e are defined radially on the entire interval $[0, +\infty]$. Second, $\widetilde{H}$ incorporates the boundary conditions at r_0 which depend on H^e. Note that this is also the case of H. The difference between $\widetilde{H}$ and H is that the former is non-Hermitian, that is although

$$\widetilde{H}|\psi(E)\rangle = E|\psi(E)\rangle \tag{28}$$

is verified, the relation

$$\langle\psi(E)|\widetilde{H} \neq E\langle\psi(E)| \tag{29}$$

also holds. As a consequence,

$$\langle\psi(E_1)|\widetilde{H}|\psi(E_2)\rangle \neq \langle\psi(E_2)|\widetilde{H}|\psi(E_1)\rangle. \tag{30}$$

This is explicitly shown in appendix A, where the difference between these two terms is calculated.

3.2. Why is it non-Hermitian?

We have just seen that the scattering (MQDT) solutions are eigenstates of a non-Hermitian Hamiltonian. From a physical point of view non-Hermiticity arises because we are considering only a *part* of the *exact* eigenstate (rather than an entire Hermitian approximation to it). This is consistent with the spirit of quantum defect theory which is not interested in and ignores the part of the wavefunction below r_0, but gives the exact wavefunctions in the outer region. However the knowledge of the wavefunction and its derivative on the boundary at $r = r_0$ is necessary. Mathematically the existence of non-vanishing boundary terms is what makes the $|\psi(E)\rangle$'s non-orthogonal, from which it follows that they are eigenstates of a non-Hermitian operator. When QDT (in the outer region) is supplemented by R-matrix computations (in the inner region) hermiticity is recovered: the exact wavefunctions are known and the boundary terms (now at $r = 0$) vanish.

Note that for continuum states the scattering eigenfunctions cannot be properly normalized, since the wavefunctions extend through an infinite radial range. The standard procedure yielding wavefunctions normalized per unit energy only depends on the asymptotic form of the free radial functions, and is thus immune to the presence of a short-range potential. It is then not necessary to worry about Hermiticity: H gives the correct expansion of the outer region Hamiltonian.

4. Working with non-Hermiticity

4.1. Biorthogonal basis

As briefly pointed out below equation (22), non-Hermiticity can potentially give rise to severe consequences and must, in a first step, be taken seriously. In a second step, we will examine whether a consistent non-Hermitian treatment brings significant differences in numerical computations.

We recall that since $\widetilde{H}$ is not Hermitian, we have

$$\widetilde{H}|\psi(E)\rangle = E|\psi(E)\rangle \tag{31}$$

and

$$\langle\psi(E)|\widetilde{H}^+ = E\langle\psi(E)|, \tag{32}$$

(so that the $|\psi(E)\rangle$ are eigenstates of $\widetilde{H}$), but contrarily to the usual (Hermitian) case, we also have

$$\langle\psi(E)|\widetilde{H} \neq E\langle\psi(E)| \tag{33}$$

and

$$\widetilde{H}^+|\psi(E)\rangle \neq E|\psi(E)\rangle. \tag{34}$$

We now introduce a biorthogonal set of functions $\{|\widetilde{\psi}(E)\rangle, |\psi(E')\rangle\}$, defined by the requirement [12]

$$\langle\widetilde{\psi}(E)|\psi(E')\rangle = \delta_{EE'}. \tag{35}$$

Employing this set we can write

$$\widetilde{H} = \sum_E E|\psi(E)\rangle\langle\widetilde{\psi}(E)| \tag{36}$$

and the adjoint reads

$$\widetilde{H}^+ = \sum_E E|\widetilde{\psi}(E)\rangle\langle\psi(E)|. \tag{37}$$

We then have

$$\langle\widetilde{\psi}(E)|\widetilde{H} = E\langle\widetilde{\psi}(E)| \tag{38}$$

and

$$\widetilde{H}^+|\widetilde{\psi}(E)\rangle = E|\widetilde{\psi}(E)\rangle, \tag{39}$$

thereby 'repairing' in a Hermitian-like fashion equations (33) and (34).

It is straightforward to formally obtain the $|\widetilde{\psi}(E)\rangle$'s from the eigenstates $|\psi(E)\rangle$. If we write the relation between $\widetilde{H}^+$ and $\widetilde{H}$ as

$$\widetilde{H} = \mathcal{G}\widetilde{H}^+\mathcal{G}^{-1}, \tag{40}$$

it can be checked that

$$|\widetilde{\psi}(E)\rangle = \mathcal{G}^{-1}|\psi(E)\rangle \tag{41}$$

$$|\psi(E)\rangle = \mathcal{G}|\widetilde{\psi}(E)\rangle, \tag{42}$$

where

$$\mathcal{G} = \sum_E |\psi(E)\rangle\langle\psi(E)| \tag{43}$$

$$\mathcal{G}^{-1} = \sum_E |\widetilde{\psi}(E)\rangle\langle\widetilde{\psi}(E)|. \tag{44}$$

By inspection it can be seen that $\mathcal{G}$ must be Hermitian. In quasi-Hermitian theories [13], $\mathcal{G}$ is often known as the metric operator, given that equation (35) is tantamount to redefining the scalar product, thereby obtaining a new Hilbert space in which the non-Hermitian Hamiltonian becomes self-adjoint. The need to introduce specific rules amounting to the redefinition of the standard scalar product appears quite naturally in non-Hermitian problems [1, 14]. We will not elaborate further on these points here (details will be given in [15]), but it must be noted that equations (36)–(44) are of common use in the growing field of PT-symmetric and pseudo-Hermitian quantum mechanics (see e.g. [16, 17] and references therein for related work).

4.2. Non-Hermitian operators and the state vectors

When calculating physical quantities with $\widetilde{H}$, $\langle\psi|$ must be replaced by $\langle\widetilde{\psi}|$ when taking the scalar product. As explained above (see also [2]), this new 'rule' is necessary to re-establish orthogonality. As a first example let us determine the average value $\langle\widetilde{H}\rangle_\chi$ where $|\chi\rangle$ is given by equations (24), (25). Let us put

$$\langle\widetilde{H}\rangle_\chi = \langle\widetilde{\chi}|\widetilde{H}|\chi\rangle. \tag{45}$$

Following equations (41) and (25) we have

$$\langle\widetilde{\chi}| = \langle\chi|\mathcal{G}^{-1} = \sum_k \alpha_k^* \langle\widetilde{\psi}(E_k)|, \tag{46}$$

and by using equations (31) or (38) along with the bi-orthonormal requirement (35), we find

$$\langle\widetilde{H}\rangle_\chi = \sum_k |\alpha_k|^2 E_k. \tag{47}$$

We have

$$\langle\widetilde{H}\rangle_\chi = \langle H^e\rangle_{\chi^e} \tag{48}$$

therefore obtaining with the outer zone Hamiltonian the same average value as the one that would have been obtained from the exact Hamiltonian (compare with $\langle H \rangle_\chi$, equation (27)).

The same rule of using $\langle \widetilde{\psi}(E) | \cdots | \psi(E) \rangle$ for the scalar product holds when computing properties of operators that are naturally expressed in terms of the eigenstates of the exact Hamiltonian H^e. The rationale is that since QDT ignores the exact solutions and only works with their outer part and associated Hamiltonian $\widetilde{H}$ which turns out to be non-Hermitian, an operator A usually expressed in terms of the $|\psi^e(E)\rangle$ should be written as a non-Hermitian operator $\widetilde{A}$ expanded on the biorthogonal basis as

$$\widetilde{A} = \sum_{EE'} |\psi(E)\rangle \widetilde{A}_{EE'} \langle \widetilde{\psi}(E')|. \tag{49}$$

Of special interest is the evolution operator. We have seen (equation (23)) that an evolution operator built from the naive outer region Hamiltonian H would not conserve probability. Indeed, $\widetilde{H}$ is not Hermitian and we should use instead

$$\widetilde{U}(t) = \sum_E e^{-iEt} |\psi(E)\rangle \langle \widetilde{\psi}(E)| \tag{50}$$

as the correct expression for the evolution operator. Of course $\widetilde{U}(t)$ cannot be unitary since $\widetilde{H}$ is not Hermitian, but is pseudo-unitary in the sense that

$$\widetilde{U}(t)\widetilde{U}^*(t) = \sum_E |\psi(E)\rangle \langle \widetilde{\psi}(E)| \equiv \widetilde{I} \tag{51}$$

where $\widetilde{I}$ plays the role of a (non-Hermitian) unit operator in conjunction with the scalar product $\langle \widetilde{\psi}(E) | \cdots | \psi(E) \rangle$, so that probability is conserved. Thus if the system is initially in the exact state $|\chi^e\rangle$ the autocorrelation function $\langle \chi^e(t=0) | \chi^e(t) \rangle$ should be written in terms of the outer region quantities as

$$\langle \widetilde{\chi} | \widetilde{U}(t) | \chi \rangle. \tag{52}$$

4.3. Physical states

In our view, the introduction of the biorthogonal basis was aimed at repairing the consequences of working with a non-Hermitian Hamiltonian in the outer region. However, from the considerations developed in section 2 we know that the exact physical eigenstates are given by $|\psi^e(E)\rangle$ which behave in the usual (Hermitian) manner. If A is a Hermitian operator corresponding to an observable and $|\chi_{\text{ph}}\rangle$ a physical state, both of which are known in a form that does not involve expansions in terms of the eigenstates of H^e, there is no need to take into account the non-Hermiticity of the outer Hamiltonian, and the usual states and scalar products should be employed. For example the mean value of the radial position operator for the outer electron in the state $|\chi_{\text{ph}}\rangle$ is given by

$$\langle R \rangle_\chi = \langle \chi_{\text{ph}} | R | \chi_{\text{ph}} \rangle. \tag{53}$$

Now even if $|\chi_{\text{ph}}\rangle$ is known on a basis independent from the Hamiltonian of the problem (e.g., a localized Gaussian state), it is still necessary to determine the form taken by $|\chi_{\text{ph}}\rangle$ on the space generated by the biorthogonal basis. In effect the time evolution or the average energy of the system in the state $|\chi_{\text{ph}}\rangle$ will necessarily bring into play the non-Hermitian Hamiltonian $\widetilde{H}$. Let us explicit different ways to represent the physical state. First the exact expansion yields

$$|\chi_{\text{ph}}^e\rangle = \sum_k \alpha_k |\psi^e(E_k)\rangle \tag{54}$$

with

$$\alpha_k = \langle \psi^e(E_k) | \chi^e_{\mathrm{ph}} \rangle \tag{55}$$

and

$$\sum_k |\alpha_k|^2 = 1. \tag{56}$$

In general the exact states $|\psi^e(E)\rangle$ and hence the exact coefficients α_k are not known. What is available is the expansion of $|\chi_{\mathrm{ph}}\rangle$ on some orthogonal basis. In principle $|\chi_{\mathrm{ph}}\rangle$ can also be expanded on the outer states $|\psi(E)\rangle$ as

$$|\chi_{\mathrm{ph}}\rangle = \sum_k a_k |\psi(E_k)\rangle \tag{57}$$

provided one keeps in mind that normalization $\langle \chi_{\mathrm{ph}} | \chi_{\mathrm{ph}} \rangle = 1$ implies that

$$\sum_k |a_k|^2 \neq 1 \tag{58}$$

since the outer states are not orthogonal. This means that the coefficients α_k and a_k are necessarily different despite $|\chi^e_{\mathrm{ph}}\rangle$ and $|\chi_{\mathrm{ph}}\rangle$ being essentially the same state. In other words, expansion (57) must not be confused with

$$|\chi\rangle = \theta(r - r_0) |\chi^e_{\mathrm{ph}}\rangle \tag{59}$$

$$= \sum_k \alpha_k |\psi(E_k)\rangle. \tag{60}$$

Note that from equation (55) we have

$$\langle \widetilde{\psi}(E_k) | \chi \rangle = \langle \psi^e(E_k) | \chi^e_{\mathrm{ph}} \rangle, \tag{61}$$

ensuring that relative to the biorthogonal basis equation (56) is still satisfied.

Equation (61) is of little help if α_k are unknown but shows that $|\chi\rangle$ and $|\chi_{\mathrm{ph}}\rangle$ are conceptually different objects. In equation (57) the outer states play the role of an alternative expansion basis, as $|\chi_{\mathrm{ph}}\rangle$ represents the physical state on the usual Hilbert space. $|\chi\rangle$ on the other hand is the restriction of the exact state to the outer region; then as seen above (e.g. equations (26) and (47)) we obtain with $|\chi\rangle$ the correct results if we use the biorthogonal basis as a mean to define a new scalar product[1]. We obtain the relation between $|\chi_{\mathrm{ph}}\rangle$ and $|\chi\rangle$ by requiring the results to be independent of the mathematical representation employed, that is for two arbitrary states $|\chi_1\rangle$ and $|\chi_2\rangle$ we should have

$$\langle \chi_{1\,\mathrm{ph}} | \chi_{2\,\mathrm{ph}} \rangle = \langle \widetilde{\chi_1} | \chi_2 \rangle. \tag{62}$$

By equation (42) this leads to

$$|\chi\rangle = \mathcal{G}^{1/2} |\chi_{\mathrm{ph}}\rangle \tag{63}$$

$$|\widetilde{\chi}\rangle = \mathcal{G}^{-1/2} |\chi_{\mathrm{ph}}\rangle, \tag{64}$$

where $\mathcal{G}$ is the metric introduced above. As a result we see that the exact expansion coefficients α can be computed from the relation

$$\alpha_k = \langle \widetilde{\psi}(E_k) | \mathcal{G}^{1/2} | \chi_{\mathrm{ph}} \rangle \tag{65}$$

although the exact eigenstates are not known.

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[1] More precisely $|\chi\rangle$ and $|\chi_{\mathrm{ph}}\rangle$ belong to different Hilbert spaces each characterized by a different inner product [13]. Finding the relation between $|\chi_{\mathrm{ph}}\rangle$ and $|\chi\rangle$ is actually tantamount to setting the mapping between these two Hilbert spaces (see [15, 16] and references therein). One must not be deceived by the fact that the same vector $|\psi(E_k)\rangle$ can belong to different Hilbert spaces.

Summarizing, if the physical state of interest is such that the exact coefficients α_k are known, then one should work right away with non-Hermitian operators in conjunction with the associated scalar product $\langle\widetilde{\psi}(E)|\cdots|\psi(E)\rangle$. Else equations (63) and (64) give the necessary connection between the states associated with the non-Hermitian operators and the physical states in the standard Hilbert space, allowing either to express the non-Hermitian operators in the standard basis, or alternatively (and a better option in practice) to obtain the physical states in the basis associated with the non-Hermitian operators; in practice this means determining the coefficients α_k.

4.4. Practical implementation

The main practical issue concerns the determination of the second basis of the bi-orthonormal set, the $|\widetilde{\psi}(E)\rangle$'s, which are formally defined through equation (41). Formally the metric $\mathcal{G}$ is a matrix of infinite rank with an unknown inverse. In practice a finite number of outer-region eigenstates $|\psi(E)\rangle$ are computed by the standard methods of quantum defect theory. We then write equation (42) as

$$|\psi(E)\rangle = \sum_{E'} \Gamma_{E'E} |\widetilde{\psi}(E')\rangle, \tag{66}$$

where

$$\Gamma_{E'E} \equiv \langle\psi(E')|\psi(E)\rangle = \langle\psi(E')|\mathcal{G}|\widetilde{\psi}(E)\rangle = \langle\widetilde{\psi}(E')|\mathcal{G}|\psi(E)\rangle \tag{67}$$

are the elements of $\mathcal{G}$ in the biorthogonal basis. These elements can be directly computed from the QDT eigenstates in the chosen range, forming the matrix Γ. We can also put equation (41) in the same form,

$$|\widetilde{\psi}(E)\rangle = \sum_{E'} \Gamma^{E'E} |\psi(E')\rangle \tag{68}$$

with

$$\Gamma^{E'E} \equiv \langle\widetilde{\psi}(E')|\widetilde{\psi}(E)\rangle = \langle\psi(E')|\mathcal{G}^{-1}|\widetilde{\psi}(E)\rangle = \langle\widetilde{\psi}(E')|\mathcal{G}^{-1}|\psi(E)\rangle. \tag{69}$$

It can be verified explicitly that the $\Gamma^{E'E}$ are the elements of the inverse matrix Γ^{-1}, i.e.

$$\sum_{E''} \Gamma_{EE''}\Gamma^{E''E'} = \delta_E^{E'}. \tag{70}$$

Therefore once the QDT eigenstates $|\psi(E)\rangle$ have been determined, the second basis elements $|\widetilde{\psi}(E)\rangle$ are obtained from equation (68) by inverting Γ. As a check, orthonormality (35) should be verified.

We also point out an approximate but less expensive manner for computing the $|\widetilde{\psi}(E)\rangle$'s which nevertheless gives acceptable results. The idea is to write $|\widetilde{\psi}(E)\rangle$ as the $|\psi(E)\rangle$ in equation (12) with unknown coefficients $\widetilde{B}_i$

$$\langle r|\widetilde{\psi}(E)\rangle = \sum_i \widetilde{B}_i(E)|i\rangle F_i(\epsilon_i, r). \tag{71}$$

The $\widetilde{B}_i(E)$'s are then found by enforcing the orthonormality relation (35) which takes the form

$$\langle\widetilde{\psi}(E)|\psi(E')\rangle = \sum_N \widetilde{B}_N^*(E) B_N(E')\langle F_N(\epsilon_N)|F_N(\epsilon_N')\rangle = \delta_{EE'}. \tag{72}$$

If there are n_i channels $|i\rangle$ then the scalar product $\langle\widetilde{\psi}(E)|\psi(E')\rangle$ is taken for n_i different functions $|\psi(E')\rangle$ centred on the energy E. This results in a linear system that is easily solved

numerically. The quality of the approximation is tested by computing $\langle \widetilde{\psi}(E)|\psi(E')\rangle$ for some values of E' lying outside the range that was explicitly employed in the linear system.

Finally, if needed, $\mathcal{G}^{1/2}$ is most easily computed from the diagonalization of $\mathcal{G}$.

5. Examples

5.1. Presentation

We will give two illustrations in which ignoring the fact that quantum defect theory is non-Hermitian produces wrong or even contradictory results. These results arise from model calculations employing a 5×5 K matrix. For definiteness we will take these calculations to correspond to a Rydberg molecule. We assume vibrations and spin can be neglected: there are only rotational channels, and the core states are labelled by the rotational number N (i.e. we have $|N\rangle$ instead of $|i\rangle$), and the core energies $E^+(N)$ depend on N. We have chosen an energy dependence for the quantum defects significantly stronger than what is found in typical atoms or molecules (where a linear or at most quadratic dependence is in order).

The first illustration involves the evolution operator: we will compute the auto-correlation function for a given wave packet that evolves according to the standard or non-Hermitian evolution operators. The second example touches upon the rôle of the density matrix: we will compute the linear entropy associated with the reduced density matrix of the system. The linear entropy quantifies entanglement and we shall see that employing the standard or non-Hermitian formulae for the density matrices can lead to significantly different results.

5.2. Wave packets: auto-correlation function

Let us suppose that initially the system is prepared in the state

$$|\psi(t=0)\rangle = |F_{\text{ini}}\rangle|N_0\rangle, \tag{73}$$

where $|F_{\text{ini}}\rangle$ is the initial radial distribution and $|N_0\rangle$ a chosen core state. We take $|F_{\text{ini}}\rangle$ to be radially localized near the outer turning point (this choice is of course arbitrary), given by

$$F_{\text{ini}}(r) = \sum_n \exp(-\mathrm{i}T_e(n_0)/2 - [(n-n_0)/2\Delta n]^2) f_L\left(\epsilon_n = \frac{-1}{2n^2}, r\right). \tag{74}$$

The $f_L(\epsilon_n, r)$ are hydrogenic radial functions appropriately normalized such that $\langle\psi(0)|\psi(0)\rangle = 1$ ($|\psi(0)\rangle$ is thus a physical state in the sense of section 4.3).

We wish to determine the autocorrelation function defined by

$$C(t) = |\langle\psi(0)|\psi(t)\rangle|. \tag{75}$$

If we disregard the issue of non-Hermiticity, we would use the standard quantum mechanical evolution operator

$$U(t) = \sum_E \mathrm{e}^{-\mathrm{i}Et}|\psi(E)\rangle\langle\psi(E)|, \tag{76}$$

yielding

$$C(t) = \left|\sum_E \mathrm{e}^{-\mathrm{i}Et}\left(B_{N_0}(E)\langle F_{N_0}(E)|F_{\text{ini}}\rangle\right)^2\right|, \tag{77}$$

where we have used equation (12) for the eigenstates with the change in notation $i \to N$. If we take into account the properties of non-Hermiticity, the relevant evolution operator is the pseudo-unitary $\tilde{U}(t)$ given by equation (47). As discussed in section 4.3 $\tilde{U}(t)$ does not act on
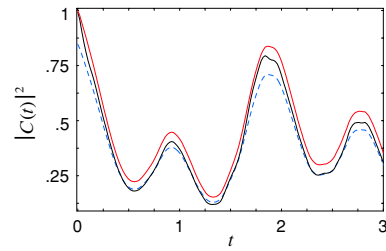
Figure 1. The autocorrelation function is given as a function of time (in units of T, the period of the mean energy Kepler orbit of the wave packet). Dashed (blue): $C(t)$, obtained by employing the propagator $U(t)$. Grey (red) solid line: renormalized $C(t)$. Black curve: $\widetilde{C}(t)$, obtained from the non-Hermitian propagator $\tilde{U}(t)$. The initial state is given by equations (73), (74) with $n_0 = 45$ and $\Delta n = 1/3$.
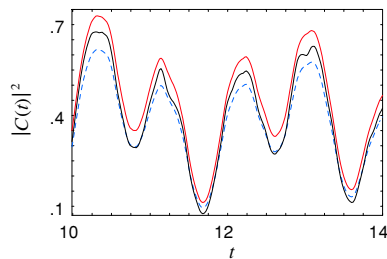
Figure 2. Same as figure 1 for longer times.

$|\psi(0)\rangle$ but on $\mathcal{G}^{1/2}|\psi(0)\rangle$, where $\mathcal{G}$ is the metric operator. The autocorrelation function that we now denote $\widetilde{C}(t)$ takes the form

$$\widetilde{C}(t) = |\langle\psi(0)|\mathcal{G}^{-1/2}\tilde{U}(t)\mathcal{G}^{1/2}|\psi(0)\rangle|. \tag{78}$$

Alternatively, the autocorrelation function can be written in non-Hermitian language as

$$\widetilde{C}(t) = |\langle\widetilde{\psi}(0)|\tilde{U}(t)|\Psi(0)\rangle|, \tag{79}$$

where we have defined $|\Psi(0)\rangle = \mathcal{G}^{1/2}|\psi(0)\rangle$ and $\langle\widetilde{\psi}(0)| = \langle\psi(0)|\mathcal{G}^{-1/2}$ (see equations (63) and (64)—beware of the change in notation!)

Here the metric was determined as explained in section 4.4 by including about 350 states $|\psi(E)\rangle$, resulting in a matrix Γ of size 350×350. The coefficients $\tilde{B}(E)$ which are necessary in order to compute the evolution operator $\tilde{U}(t)$ were obtained by inverting Γ. Note that $\widetilde{C}(t)$ is expected to be different from $C(t)$ if the non-diagonal elements of Γ are not negligible.

Figure 1 shows the autocorrelation functions $C(t)$ (dashed) and $\widetilde{C}(t)$ (black solid) for short times. In particular note that $C(t = 0) \approx 0.85$ is well below the value of 1 expected from normalization, although $|\psi(0)\rangle$ is normalized to 1: this is due to the fact $U(t = 0)$ as given by equation (76) is not the proper unit operator and spoils orthonormality. This is why we have also plotted the renormalized curve $C(t)/C(t = 0)$, which nevertheless does not match $\widetilde{C}(t)$ better than $C(t)$. Note that the profiles of the curves are different: this is particularly clear in figure 2 where the same autocorrelation functions are plotted at longer times. We recall in this respect that autocorrelation functions are quantities that can be experimentally observed.

5.3. Entanglement production: linear entropy

As is obvious from equation (12), a molecular eigenstate consists of a superposition of entangled core-outer electron states (here the term 'core' actually includes the orbital degrees of freedom of the electron). This is even more the case of a wave packet, formed by the superposition of several eigenstates. To quantify the degree of bipartite entanglement, it is a standard practice to compute the linear entropy S_2 associated with the reduced density matrix of the system. S_2 is zero for product (non-entangled) states and reaches a maximal value $S_2^{\max} = (p-1)/p$ for maximally entangled states (p is the maximum number of independent product states available to the system; see [18] for a general overview, [19] for the discussion of entanglement in Rydberg molecules).

We will assume we initially have a product state, e.g. the one given by equations (73), (74). Let $|\psi(t)\rangle$ be the wavefunction at time t and

$$\rho(t) = |\psi(t)\rangle\langle\psi(t)| \tag{80}$$

the density matrix of the system. The reduced density matrix $\rho_e(t)$ is obtained by averaging over the core degrees of freedom

$$\rho_e(t) = \mathrm{Tr}_N \rho(t) = \sum_N \langle N|\rho(t)|N\rangle. \tag{81}$$

Recall that normalization and the conservation of probability imply that

$$\mathrm{Tr}\,\rho(t) = \mathrm{Tr}_e \rho_e(t) = 1. \tag{82}$$

The linear entropy is then defined as

$$S_2(t) = 1 - \mathrm{Tr}_e \rho_e^2(t), \tag{83}$$

where

$$\mathrm{Tr}_e \rho_e^2(t) = \int \langle r|\rho_e^2|r\rangle r^2 \, dr. \tag{84}$$

These formulae are valid in standard quantum mechanics. If we attempt to apply them naïvely here as if the QDT basis were orthonormal, we get the following results. We first expand the eigenstates as

$$|\psi(0)\rangle = \sum_k c(E_k)|\psi(E_k)\rangle \tag{85}$$

with $c(E_k) = \langle\psi(E_k)|\psi(0)\rangle$ (which is already an incorrect manipulation). We then apply the evolution operator $U(t)$ and trace over $|N\rangle$ to find

$$\rho_e(t) = \sum_{EE'} \mathrm{e}^{-\mathrm{i}(E-E')t} c^*(E') c(E) \sum_N B_N^*(E') B_N(E) |F_N(\epsilon_N)\rangle\langle F_N(\epsilon'_N)|, \tag{86}$$

where we have used equation (12) for the eigenstates with the change in notation $i \to N$. It is straightforward to take the trace over $|r\rangle$; it may be noted that

$$\mathrm{Tr}_e \rho_e(t) \neq 1, \tag{87}$$

meaning that probability is not conserved. This is illustrated in figure 3, where this quantity is plotted as a function of time (we take the same states used in the determination of the autocorrelation function above). We see that this non-conservation is not negligible. The linear entropy is then computed from equation (83) and plotted in figure 4. As for the autocorrelation function, we have also plotted the renormalized linear entropy defined here by

$$S_2^{\mathrm{renorm}}(t) = 1 - \frac{\mathrm{Tr}_e \rho_e^2(t)}{[\mathrm{Tr}\,\rho(t)]^2}.$$
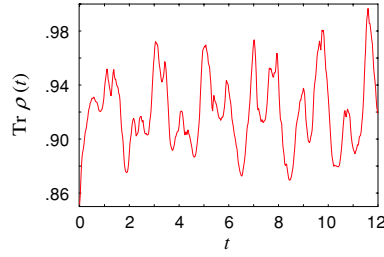
Figure 3. Formally the time conservation of the probability and the normalization follow from $\mathrm{Tr}\,\rho(t) = 1$. The curve shows $\mathrm{Tr}\,\rho(t)$ as computed from equation (86), which is neither equal to 1 nor constant in time, contrarily to the non-Hermitian $\mathrm{Tr}\,\widetilde{\rho}(t)$ (see equation (91)). t is given in units of T.
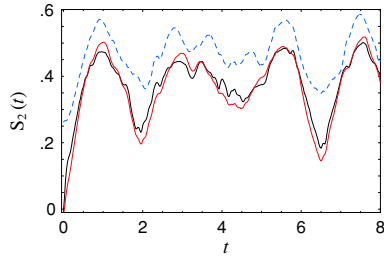
Figure 4. The linear entropy associated with the reduced density matrix ρ_e is plotted as a function of time (in units of the mean Kepler period T). Dashed (blue) curve: $S_2(t)$ obtained by ignoring the non-Hermiticity of the Hamiltonian. Grey (red) solid line: $S_2^{\mathrm{renorm}}(t)$, i.e. the renormalized version of $S_2(t)$, defined by equation (92). Black curve: $\widetilde{S}_2(t)$, obtained from the non-Hermitian density matrix $\widetilde{\rho}(t)$.

The linear entropy is renormalized at each instant to counter the non-physical non-conservation of probability.

We now determine the same quantities by explicitly caring for non-Hermiticity. The initial state becomes

$$|\Psi(0)\rangle = \mathcal{G}^{1/2}|\psi(0)\rangle = \sum \alpha(E_k)|\psi(E_k)\rangle \tag{88}$$

its dual $\langle\widetilde{\psi}(0)|$ and the density matrix

$$\widetilde{\rho}(t) = |\Psi(t)\rangle\langle\widetilde{\Psi}(t)| \tag{89}$$

with the evolution operator $\tilde{U}(t)$ given by equation (47). Tracing over $|N\rangle$ we find

$$\widetilde{\rho}_e(t) = \sum_{EE'} e^{-i(E-E')t}\alpha^*(E')\alpha(E)\sum_N \widetilde{B}_N^*(E')B_N(E)|F_N(\epsilon_N)\rangle\langle F_N(\epsilon_N')|. \tag{90}$$

Taking the trace over $|r\rangle$ and using the orthogonality property as given in equation (72) leads to

$$\mathrm{Tr}_e\,\widetilde{\rho}_e(t) = \sum_E |\alpha(E)|^2 = 1. \tag{91}$$

The equality hold strictly by virtue of equation (56), which enforces conservation of probability; in practice the precision obtained depends on the precision chosen to compute the eigenvectors and the metric. The linear entropy

$$\widetilde{S}_2(t) = 1 - \mathrm{Tr}_e\,\widetilde{\rho}_e^2(t) \tag{92}$$

is shown in figure 4 along with S_2 and S_2^{renorm}. $\widetilde{S}_2$ and S_2 are significantly different. It may be noted that $S_2(t = 0) \approx 0.25$ instead of 0, which should be the value of the linear entropy for the unentangled initial state. The renormalized curve $S_2^{\text{renorm}}(t)$ matches better $\widetilde{S}_2(t)$ (whereas for the autocorrelation functions we saw the renormalized curve was a worse approximation).

6. Discussion and conclusion

We have shown above that QDT is non-Hermitian, seen how this non-Hermiticity can be explicitly accounted for and finally illustrated numerically the errors made when non-Hermiticity issues are ignored when computing the evolution operator. We now wish to assess under which circumstances the errors made by ignoring non-Hermiticity are numerically relevant. Indeed, to our knowledge, non-Hermitian aspects of quantum defect theory were not discussed previously; for instance in numerous investigations of Rydberg wave packets (e.g. [20]), the standard evolution operator $U(t)$ was employed. Unsurprisingly we will conclude that in most circumstances non-Hermitian features can rightly be neglected.

There is no doubt that formally quantum defect theory is non-Hermitian. As stressed in this work non-hermiticity does not entail that the eigenfunctions and eigenenergies obtained by QDT are incorrect but that the expansions of states and operators involving the eigenfunctions should be done in principle by using a biorthogonal basis. By doing so, one repairs the consequences of dealing with a non-Hermitian Hamiltonian in the outer region. This is readily apparent in the simplest example we have given dealing with the computation of the average value of the Hamiltonian (see section 4.2). However in practice there are several other issues that may play a more important role, so that the corrections brought by the use of the biorthogonal basis may turn out to be insignificant.

First, note that the continuum eigenstates do not suffer from non-Hermiticity: they are perfectly orthogonal and form a basis for expanding Hermitian operators. Therefore when emphasis is put in the continuum such as in investigations of autoionizing wave packets, non-Hermiticity can safely be ignored; the resonances' positions depend on the eigenvalues (which are immune to non-Hermitian issues) and their profile depend on quantities such as transition probabilities or pulse characteristics which are computed with errors that are higher than the errors made by ignoring non-Hermiticity. Even for pure bound state excitations, the degree to which the formalism is effectively non-Hermitian transpires in the non-orthogonality of the eigenstates given by equation (21) (we can actually be more precise and define a non-Hermiticity index, see [15]). For energy-independent quantum defects, the orthogonality relation (21) may be taken to hold for all practical purposes: the error made in doing so is the same that is made by neglecting the energy dependence of the functions f and g for small r (see appendix A), typically well below 10^{-6} even for low quantum numbers. When the reaction matrix K is energy dependent, orthogonality of the eigenfunctions cannot hold as a matter of principle, given that each eigenfunction is a solution of a different effective Hamiltonian. Typically, the energy dependence is small, and in the tests we made, non-orthogonality of two eigenstates seldom goes above 10^{-2} for the highest values (and below 10^{-4} for most scalar products of eigenvectors). For a stronger energy dependence of the quantum defects non-orthogonality can rise well beyond 10%, and it then becomes necessary to account for non-Hermiticity. The examples given in this work fall in this case. Note that the relevant energy dependence is that of the overall K-matrix employed when the boundary conditions are taken; in most Rydberg problems the short-range quantum defects have a simple energy dependence, but the K-matrix mixes these quantum defects and their simple energy dependences through a frame transformation.

To conclude, it seems likely that in most circumstances ignoring the non-Hermitian nature of the quantum defect theory Hamiltonian will not give manifestly wrong results. Still, it is important to be aware that non-Hermiticity may need to be accounted for, in particular when studying the time evolution of bound wave packets with a strong energy dependence of the scattering process, as illustrated in this work.

Acknowledgments

Appendix A

We will consider $\widetilde{H}$, that is H_0 as given by equation (2), on the interval $[r_0, +\infty]$. Let us first compute the radial elements

$$\left\langle F_i(\epsilon_1) \left| \frac{p_r^2}{2} \right| F_i(\epsilon_2) \right\rangle \tag{A.1}$$

and

$$\left\langle F_i(\epsilon_2) \left| \frac{p_r^2}{2} \right| F_i(\epsilon_1) \right\rangle \tag{A.2}$$

on $[r_0, +\infty]$. Integrating by parts, we have e.g.

$$\left\langle F_i(\epsilon_1) \left| \frac{p_r^2}{2} \right| F_i(\epsilon_2) \right\rangle = -\frac{1}{2} F(r, \epsilon_1) \partial_r F(r, \epsilon_2) \Big|_{r=r_0} + \frac{1}{2} \int_{r_0}^{+\infty} \partial_r F(r, \epsilon_1) \partial_r F(r, \epsilon_2) \, dr \tag{A.3}$$

and thus

$$\left\langle F_i(\epsilon_1) \left| \frac{p_r^2}{2} \right| F_i(\epsilon_2) \right\rangle - \left\langle F_i(\epsilon_2) \left| \frac{p_r^2}{2} \right| F_i(\epsilon_1) \right\rangle = \frac{1}{2} W[F_i(\epsilon_2), F_i(\epsilon_1)], \tag{A.4}$$

where $W[a, b] = a \partial_r b - b \partial_r a$ is the Wronskian. We now use equation (13) and the well-known fact [5] that near the origin the Coulomb functions f and g do not depend on the energy (since their behaviour is determined by the singularity at $r = 0$). Sticking to the standard choice $W[f, g] = 2/\pi$ employed in QDT, we find

$$\left\langle F_i(\epsilon_1) \left| \frac{p_r^2}{2} \right| F_i(\epsilon_2) \right\rangle - \left\langle F_i(\epsilon_2) \left| \frac{p_r^2}{2} \right| F_i(\epsilon_1) \right\rangle = \frac{1}{\pi \nu_1^{3/2} \nu_2^{3/2}} \sin[\beta_i(\epsilon_2) - \beta_i(\epsilon_1)]. \tag{A.5}$$

As an aside, we note that to recover equation (22), obtained [11] from

$$\langle F_i(\epsilon_1) | F_i(\epsilon_2') \rangle = \frac{W[F_i(\epsilon_2), F_i(\epsilon_1)]}{\epsilon_2 - \epsilon_1}, \tag{A.6}$$

a further approximation $\nu_1^{3/2} \nu_2^{3/2} \approx \nu^3$ should be used, where ν lies in between ν_1 and ν_2 and cancels out of the final expression for $\langle F_i(\epsilon_1) | F_i(\epsilon_2) \rangle$ by making the same approximation for $\epsilon_2 - \epsilon_1$. For sufficiently high quantum numbers this approximation brings an error which is of the same order of magnitude as the one made by neglecting the energy dependence of f and g near r_0 and is therefore justified. We now use equation (A.6) to compute

$$\langle \psi(E_1) | \widetilde{H} | \psi(E_2) \rangle - \langle \psi(E_2) | \widetilde{H} | \psi(E_1) \rangle. \tag{A.7}$$

Since the V_{LR} and H_0^{core} terms of equation (2) vanish when the difference (A.7) is taken, and since $\langle i|j\rangle = \delta_{ij}$, only the terms of the form (A.5) contribute, yielding

$$\langle\psi(E_1)|\widetilde{H}|\psi(E_2)\rangle - \langle\psi(E_2)|\widetilde{H}|\psi(E_1)\rangle = \frac{1}{\pi\nu_1^{3/2}\nu_2^{3/2}}\sum_i B_i(E_1)B_i(E_2)\sin[\beta_i(\epsilon_2) - \beta_i(\epsilon_1)].$$

(A.8)

Hence the fact that p_r^2 is not Hermitian on $[r_0, +\infty]$ gives rise to a non-Hermitian Hamiltonian.

Note that if we use $\widetilde{H}|\psi(E)\rangle = E|\psi(E)\rangle$ in equation (A.7), we get

$$\langle\psi(E_1)|\widetilde{H}|\psi(E_2)\rangle - \langle\psi(E_2)|\widetilde{H}|\psi(E_1)\rangle = \sum_i B_i(E_1)B_i(E_2)\{\langle F_i(\epsilon_1)|F_i(\epsilon_2)\rangle(E_2 - E_1)\}.$$

(A.9)

The term between braces is exactly equal to $W[F_i(\epsilon_2), F_i(\epsilon_1)]/2$, naturally giving the same result (A.8).

References

[1] Gilary I, Fleischer A and Moiseyev N 2005 *Phys. Rev.* A **72** 012117
[2] Faisal F H M and Moloney J V 1981 *J. Phys. B: At. Mol. Phys.* **14** 3603
[3] Bloch C 1957 *Nucl. Phys.* **4** 503
[4] Burke P G, Hibbert A and Robb W D 1971 *J. Phys. B: At. Mol. Phys.* **4** 153
[5] Seaton M J 1983 *Rep. Prog. Phys.* **46** 167
[6] Fano U and Rau A R P 1986 *Atomic Collisions and Spectra* (Orlando: Academic)
[7] Yeazell J A and Uzer T (ed) 2000 *The Physics and Chemistry of Wave Packets* (New York: Wiley-Interscience)
[8] Fano U 1978 *Phys. Rev.* A **17** 93
[9] Labastie P and Jalbert G 1992 *Phys. Rev.* **46** 2581
[10] Matzkin A 1999 *Phys. Rev.* A **59** 2043
[11] Bell R H and Seaton M J 1985 *J. Phys. B: At. Mol. Phys.* **18** 1589
[12] Morse P M and Feshbach H 1953 *Methods of Theoretical Physics* (New York: McGraw-Hill)
[13] Scholtz F G, Geyer H B and Hahne F J W 1992 *Ann. Phys.* **213** 74
[14] Moiseyev N 1998 *Phys. Rep.* **302** 211
[15] Matzkin A 2006 *J. Phys. A: Math. Gen.* **39** 10859
[16] Mostafazadeh A and Batal A 2004 *J. Phys. A: Math. Gen.* **37** 11645
[17] Znojil M 2004 *Phys. Lett.* A **326** 70
[18] Nielsen M A and Chuang I L 2000 *Quantum Computation and Quantum Information* (Cambridge: Cambridge University Press)
[19] Lombardi M and Matzkin A 2006 *Europhys. Lett.* **74** 771
[20] Robicheaux F and Hill W T 1996 *Phys. Rev.* A **54** 3276
Lyons B J, Schumacher D W, Duncan D I, Jones R R and Gallagher T F 1998 *Phys. Rev.* A **57** 3712
Texier F and Jungen Ch 1999 *Phys. Rev.* A **59** 412
Smith R A L, Stavros V G, Verlet J R R, Fielding H H, Townsend O and Softley T P 2003 *J. Chem. Phys.* **119** 3085