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Green's functions for separable potentials

Søren Berg Padkjær, Esper Dalgaard

Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

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Summary. The convergence properties of approximate one-particle Green's functions derived from separable potential expansions are examined. A convergence criterion for the basis set to be used in a Löwdin-type inner projection is established and illustrated by calculations of matrix elements of the Coulomb Green's function based on separable potentials of finite rank. It is then suggested that a separable potential ansatz for a many-electron wave function may be introduced into Frenkel's time-dependent variation principle in order to obtain approximate response functions with the continuum of one-particle states explicitly included. A preliminary outline of the formalism at the time-dependent Hartree–Fock level is presented.

Key words: Separable potentials – Continuum states – Green's functions – Frenkel's variation principle

1. Introduction

It is quite generally apparent from intermediate and advanced textbooks on quantum mechanics and its applications to the calculation of atomic and molecular response properties that sums over states, which include the integration over the continuum manifold of one-particle states are called for. Such summations may be carried out, if the one-particle Green's functions are known [1]. As it is well known, however, there are only very few examples of systems for which accurate Green's functions are available, and even in the simple case of a hydrogen-like Coulomb potential, the analytic form [2] is too complicated to encourage molecular applications, even if the matrix elements are known explicitly in a Slater basis [3].

An approximation scheme, which is based on separable one-particle potentials needed for the treatment of many-electron response properties, is considered in this paper with the view of determining response functions, which includes the continuum in an explicit manner. We shall write a separable potential of finite rank, n, as

$$v_n(x, x') = \sum_1^n \theta_s(x) a_{ss'} \theta_{s'}(x')^*, \tag{1}$$

where $\boldsymbol{a} = \{a_{ss'}\}$ is a Hermitian matrix of dimension n, and $\{\theta_s(x)\}$ denotes a suitable set of basis functions for the potential. The combined space-spin variables for one electron are written as $x = (\boldsymbol{r}, \zeta)$. An outline of the mathematical properties of separable potentials was given by Ghirardi and Rimini [4]. They showed, that while the number of bound states derived from the Schrödinger equation corresponding to such potentials at most equals the number of negative eigenvalues of the matrix $\boldsymbol{a}$, the total manifold of bound and continuum states is complete. We shall in particular consider separable potentials derived by using Löwdin's inner projections [5].

The separable potential offers an explicit expression for the associated Green's function, which should satisfy the equation

$$\{E + \tfrac{1}{2}\Delta\}\; G_n(x, x'; E) = \delta(x - x') + \int \mathrm{d}x''\, v_n(x, x'')G_n(x'', x'; E) \tag{2}$$

for a generally complex value of the energy variable E with the appropriate boundary conditions. As an auxiliary tool we employ the free particle Green's function $G_0(E)$ for which we have the differential equation

$$\{E + \tfrac{1}{2}\Delta\}\; G_0(x, x'; E) = \delta(x - x'). \tag{3}$$

Provided that the boundary conditions imposed on Eqs. (2) and (3) are the same, the solution to Eq. (2) may be written as

$$\begin{aligned} G_n(E) &= G_0(E) + G_0(E)|\theta\rangle \boldsymbol{a}[\mathbf{1} - \boldsymbol{T}(E)\boldsymbol{a}]^{-1}\langle\theta|G_0(E) \\ &= G_0(E) + G_0(E)|\theta\rangle[\boldsymbol{a}^{-1} - \boldsymbol{T}(E)]^{-1}\langle\theta|G_0(E) \end{aligned} \tag{4}$$

in a compact operator notation. We have introduced here a matrix representation, $\boldsymbol{T}(E)$, of the free particle Green's function in the basis $\{\theta_s(x)\}$, i.e.

$$\boldsymbol{T}(E) = \langle\theta|G_0(E)|\theta\rangle. \tag{5}$$

The algebra used to derive Eq. (4) is well known [6]. The last step is of course only valid, when the matrix $\boldsymbol{a}$ is non-singular.

The approach to response function calculations, which we adopt here, is formally closely related to the use of Schwinger's variation principle in scattering theory [7] and Hall's variation principle for bound states [8] as generalized by Thulstrup et al. [9]. Operator kernels such as those given by Eq. (4) are sufficiently explicit and manageable to make molecular applications feasible. Several calculations concerning electron scattering on molecules have demonstrated this fact [7].

The convergence properties of a sequence of approximate one-particle Green's functions derived from separable expansions for the potential of increasing rank are examined in the next section, where a convergence criterion for the basis set to be used in a Löwdin-type inner projection is established. The method is illustrated by calculations of matrix elements of approximate Coulomb Green's functions in Sect. 3, which includes suggestions for possible improvements. Orbital variations generated by variations in a separable potential are then considered in the fourth and final section of this paper. The results indicate that a separable potential may be introduced as an *ansatz* into Frenkel's time-dependent variation principle in order to obtain approximate response functions with the continuum of one-particle states included in a closed form. A preliminary outline of the formalism is given.

2. Approximate matrix elements of Coulomb Green's functions

Consider the following pair of equations:

$$\{E + \tfrac{1}{2}\Delta - v(x)\}\, G(x, x'; E) = \delta(x - x') \tag{6}$$

and

$$\{E + \tfrac{1}{2}\Delta - v_n\}\, G_n(x, x'; E) = \delta(x - x') \quad (n = 1, 2, \dots). \tag{7}$$

In Eq. (6) v denotes an ordinary local, negative-definite Coulomb potential, and the operator v_n is given by the inner projection

$$v_n = -(-v)^{1/2} Q_n (-v)^{1/2}, \tag{8}$$

where we have introduced the projection operator

$$Q_n = \sum_{1}^{n} |\omega_s\rangle\langle\omega_s| \tag{9}$$

for an n-dimensional subspace of L^2, spanned by the orthonormal set $\{\omega_s\}$.

Due to the particular asymptotic features of the Coulomb Green's function, we do not anticipate a pointwise convergence of the sequence $\{G_n(x, x'; E)\}$ toward $G(x, x'; E)$ when the free particle Green's function is used as G_0 in Eq. (4). Instead, we shall focus the attention on the possible convergence properties in the weak sense [10]. Thus, we wish to prove that under certain conditions it holds that

$$\lim_{n\to\infty} \langle\phi|G_n(E)|\phi\rangle = \langle\phi|G(E)|\phi\rangle \tag{10}$$

for a square-integrable test function $\phi(x)$, i.e.

$$\|\phi\|^2 = \int \mathrm{d}x\, |\phi(x)|^2 < \infty. \tag{11}$$

The test function clearly belongs to the domain of both the operators $G(E)$ and $G_n(E)$. Furthermore, we have the inequality

$$\|G\phi\| \leqslant \|\phi\|/\eta \tag{12}$$

(and a similar one for $\|G_n\phi\|$) where the real parameter η is defined as the distance between the complex point E and the closest singularity of G, i.e.

$$\eta = \inf\{|E - \varepsilon|, \quad \text{where } \varepsilon \in \text{the spectrum of } -\tfrac{1}{2}\Delta + v(x)\}. \tag{13}$$

We shall assume throughout that the energy variable is chosen such that $\eta > 0$.

It follows from Eq. (6) that

$$\{E + \tfrac{1}{2}\Delta - v_n\} G(E)|\phi\rangle = |\phi\rangle + (v - v_n) G(E)|\phi\rangle. \tag{14}$$

Forming the scalar products on both sides of Eq. (14) with the function $G_n^+\,|\phi\rangle$ and using Eq. (7) with E replaced by E^* we find that

$$\langle\phi|G - G_n|\phi\rangle = \langle G_n^+\,\phi|(v - v_n) G|\phi\rangle. \tag{15}$$

We consider first the somewhat simpler case, in which the singularity at the origin of the Coulomb potential is removed by assigning a finite radius to the nucleus, such that

$$\mu = \sup\{-v(\boldsymbol{r}) \mid \boldsymbol{r} \in R^3\} < \infty. \tag{16}$$

It is convenient to introduce the notation

$$|\psi_n\rangle = (-v)^{1/2} G_n(E) |\phi\rangle \tag{17}$$

and

$$|\psi\rangle = (-v)^{1/2} G(E) |\phi\rangle. \tag{18}$$

We assume that the test function is sufficiently well behaved to ensure that both of these functions belong to L^2. This is not a serious limitation since the boundary conditions on the Coulomb Green's function ascertains that $\boldsymbol{r}\psi$ is zero at the origin [2].

Then Eq. (15) may be rewritten as

$$\langle \phi | G - G_n | \phi \rangle = -\langle \psi_n | (1 - Q_n) | \psi \rangle \tag{19}$$

and an application of the Cauchy–Schwartz inequality gives

$$\begin{aligned} |\langle \phi | G(E) - G_n(E) | \phi \rangle| &\leqslant \|\psi_n\| \, \|(1 - Q_n)\psi\| \\ &\leqslant \mu^{1/2} \eta^{-1} \|\phi\| \, \|(1 - Q_n)\psi\| \to 0 \quad \text{when } n \to \infty, \end{aligned} \tag{20}$$

provided that the basis set $\{\omega_s\}$ is complete, and we conclude that Eq. (10) is valid in this case.

In the case of one-point charge singularity in the potential at the origin we first apply the Cauchy–Schwartz inequality to Eq. (15):

$$\begin{aligned} |\langle \phi | G(E) - G_n(E) | \phi \rangle| &\leqslant \|G_n^+ \phi\| \, \|(v - v_n) G\phi\| \\ &\leqslant \|\phi\| \, \|(v - v_n) G\phi\| \eta^{-1} \end{aligned} \tag{21}$$

Thus, we examine the norm of the function $(v - v_n)G\phi$. Let ω and Ω denote the unit sphere around the origin and its complement, respectively, such that

$$R^3 = \omega \cup \Omega. \tag{22}$$

Also, let

$$\rho = \sup\{-v(\boldsymbol{r}); \boldsymbol{r} \in \Omega\}. \tag{23}$$

Then we find that

$$\begin{aligned} \|(v - v_n) G\phi\|^2 &= \int \mathrm{d}x \, |(v - v_n) G\phi|^2 \\ &= \int \mathrm{d}x \, (-v(\boldsymbol{r})) |(1 - Q_n)\psi|^2 \\ &= \Gamma_n + \Delta_n, \end{aligned} \tag{24}$$

where ψ is defined by Eq. (18) and we have introduced the quantities

$$\Gamma_n = \int_\omega \mathrm{d}x \, (-v(\boldsymbol{r})) |(1 - Q_n)\psi|^2 \tag{25}$$

and

$$\begin{aligned}\Delta_n &= \int_\Omega \mathrm{d}x\,(-v(\boldsymbol{r}))|(1-Q_n)\psi|^2\\ &\leqslant \rho\int_\Omega \mathrm{d}x\,|(1-Q_n)\psi|^2\\ &\leqslant \rho\,\|(1-Q_n)\psi\|^2 \to 0 \quad \text{when } n\to\infty.\end{aligned} \tag{26}$$

For any positive, real number α, the Coulomb potential admits the definition of a positive, finite parameter, $\lambda(\alpha)$, as the integral

$$\lambda(\alpha) = \int_\omega \mathrm{d}x\,(-v(\boldsymbol{r}))r^{(2\alpha-2)} < \infty. \tag{27}$$

By rewriting Eq. (25) we find that

$$\begin{aligned}\Gamma_n &= \int_\omega \mathrm{d}x\,(-v(\boldsymbol{r}))r^{(2\alpha-2)}|r^{1-\alpha}(1-Q_n)\psi|^2\\ &\leqslant \lambda(\alpha)\sup\{|r^{1-\alpha}(1-Q_n)\psi(x)|^2;\,\boldsymbol{r}\in\omega,\,\zeta=1,\,-1\},\end{aligned} \tag{28}$$

Thus, we conclude that the separable potential approximation scheme for bound state matrix elements of the Coulomb Green's function considered here is convergent provided that an $\alpha > 0$ exists such that

$$\lim_{n\to\infty}\,\sup\{|r^{1-\alpha}(1-Q_n)(-v)^{1/2}G(E)\phi(x)|^2;\,\boldsymbol{r}\in\omega,\,\zeta=1,\,-1\}=0. \tag{29}$$

This type of uniform convergence is to be viewed as a requirement on the basis set, which we employ in the inner projection given by Eq. (9). The convergence criterion given here is readily generalized to a general molecular nuclear framework.

3. Test calculations

In order to test the numerical aspects of the convergence given by Eq. (10), we have carried out some matrix element calculations for the simple hydrogenic potential $-1/\boldsymbol{r}$ for various choices of test functions, ϕ.

All example calculations presented in this section are carried out in spherical symmetry in which case we have the usual decomposition [11]

$$G(x,x';E) = \delta_{\zeta\zeta'}\sum_0^\infty g^l(r,r';E)/rr'\{P_l(\cos\theta)(2l+1)/4\pi\} \tag{30}$$

and similar ones for the separable potential- and free particle Green's functions. The partial wave components of the latter are given by

$$g_0^l(r,r';E) = (4/\pi)\int_0^\infty \mathrm{d}k\,(kr)j_l(kr)(kr')j_l(kr')/(2E-k^2), \tag{31}$$

where $j_l(kr)$ denotes an ordinary spherical Bessel function.

In spherical symmetry Eq. (1) adopts the following form:

$$v_n(x, x') = \delta_{\zeta\zeta'} \sum v^l(r, r')/rr' \{P_l(\cos\theta)(2l+1)/4\pi\}, \tag{32}$$

where

$$v^l(r, r') = \sum r^{-1/2}\omega(jl, r)r'^{-1/2}\omega(j'l, r')^* a_{jj'} \quad (j, j' = 1, 2, \ldots, n), \tag{33}$$

with one a-matrix for each value of l. Each angular momentum component of the separable potential Green's function can then be written in the same form as given by Eq. (4):

$$g^l(r, r'; E) = g_0^l(r, r'; E) + \sum \kappa_j^l(r; E)[\boldsymbol{a}^{-1} - \boldsymbol{T}(E)]_{jj'}^{-1} \kappa_{j'}^l(r'; E^*)^*. \tag{34}$$

We have introduced the functions

$$\kappa_j^l(r; E) = (4/\pi)\int_0^\infty \mathrm{d}k\,(kr)j_l(kr)\theta_j^l(k)/(2E - k^2), \tag{35}$$

where

$$\theta_j^l(k) = \int_0^\infty \mathrm{d}r\,(kr)j_l(kr)r^{-1/2}\omega(jl, r). \tag{36}$$

The matrix elements of the T-matrix are given by

$$T_{jj'}^{\,l}(E) = (4/\pi)\int_0^\infty \mathrm{d}k\,\theta_j^l(k)^*\theta_{j'}^l(k)/(2E - k^2). \tag{37}$$

These equations allow us to evaluate the left-hand side of Eq. (10) for any value of E. We are frequently interested in taking the limit $E = \omega + i\eta \rightarrow \omega + i0^+$, and when matrix elements for real energy values are reported in the following, this limiting procedure is implicitly understood. While the validity of Eq. (10) of course not implies, that the two limiting procedures may be interchanged, we have only encountered one case, $\omega = 0$, for which a problem arises in this regard. We shall return to this question shortly.

From the generalized Hall variation principle [9] we know that rapid convergence for bound state singularities of $G_n(E)$ toward the exact values can be expected as the number of basis functions is increased. The findings of the present study confirm this expectation without exception, but there is no reason to exhibit such well known results here.

Consider now the matrix element on the right-hand side of Eq. (10), which has the spectral representation,

$$\langle\phi|G(E)|\phi\rangle = \sum |\langle\phi|nlm\nu\rangle|^2/(E - \varepsilon_{nl}) + \int_0^\infty \rho(\varepsilon, l)\,\mathrm{d}\varepsilon|\langle\phi|\varepsilon lm\nu\rangle|^2/(E - \varepsilon), \tag{38}$$

where $(nlm\nu)$ and $(\varepsilon lm\nu)$ label bound and scattering states, respectively, and ρ denotes the density of states. A series of calculations using $1s$ type of test function, i.e. (suppressing spin)

$$\phi(\boldsymbol{r}) = 2\zeta^{3/2}\exp(-\zeta r)Y_{00}(\theta, \phi), \tag{39}$$

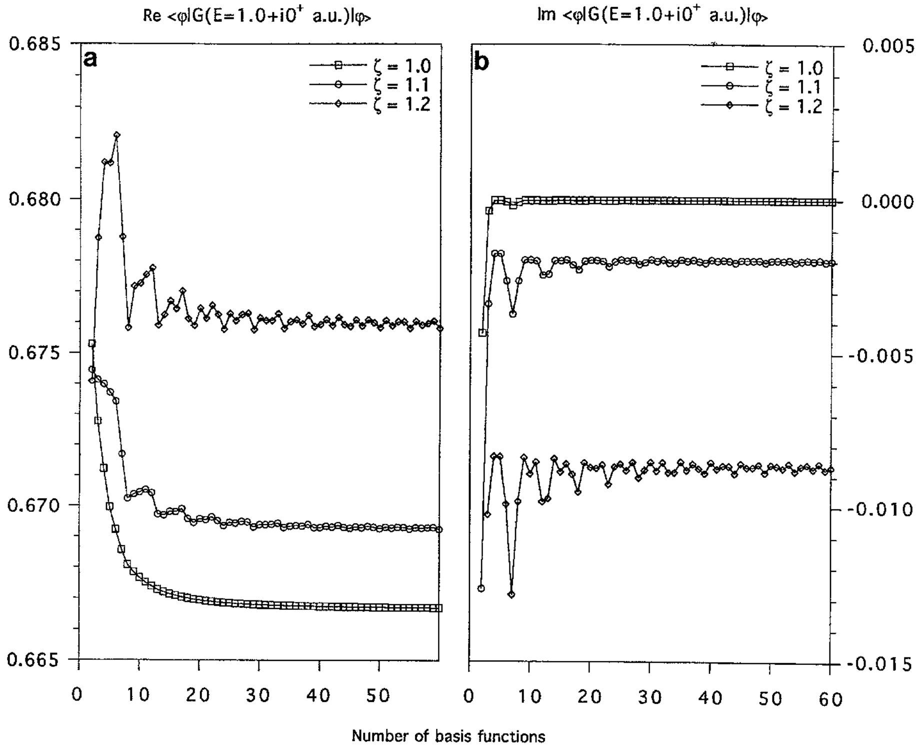

Fig. 1. Separable potential Green's function matrix element at $E = 1.0 + i0^+$ a.u. using a 1s Slater orbital with exponent ζ as a test function versus the number of basis functions

with different exponents are exhibited in Fig. 1. For these calculations the L^2-basis used in the inner projection given by Eq. (8) was chosen as

$$\omega(j0, r) = [8/(j + 1)(j + 2)]^{1/2} r L_j^{(2)}(2r) \exp(-r), \tag{40}$$

where $L_j^{(2)}$ denotes a generalized Laguerre polynomial. The radial functions $\{\omega(j0, r) \mid j = 1, \ldots, n)\}$ are orthonormal and the a-matrix in Eq. (33) becomes minus one times the unit matrix. Convergence, in the sense

$$\lim_{n \to \infty} \langle \phi | G_n(\omega + i0^+) | \phi \rangle = \langle \phi | G(\omega + i0^+) | \phi \rangle \tag{41}$$

which is not an immediate consequence of Eq. (10), is achieved for both the real and imaginary parts of the matrix element, but with the chosen basis set a relatively large number of functions is needed. The test function given by Eq. (39) generally has a non-vanishing overlap with both the bound and continuum eigenfunctions in Eq. (38), but when $\zeta = 1.00$, ϕ becomes the exact 1s eigenfunction so that

$$\langle \phi | G(\omega + i0^+) | \phi \rangle = (\omega + \tfrac{1}{2})^{-1}, \tag{42}$$

which provides a simple check on the results. We note that the imaginary part of the matrix element converges very rapidly toward zero at $E = 1.0 + i0^+$ as it is apparent from Fig. 1b.

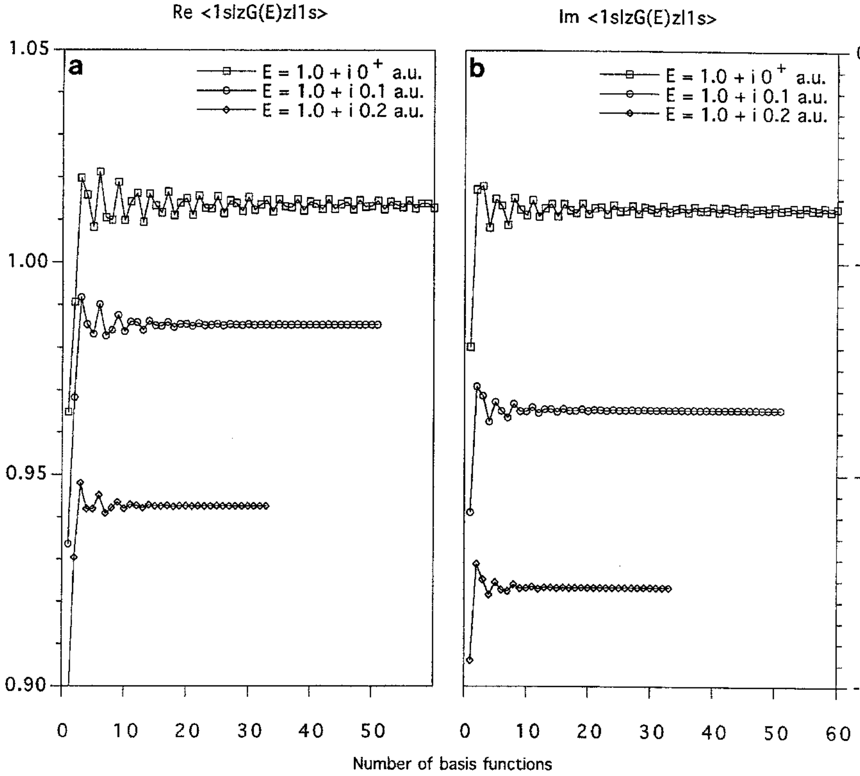

Fig. 2. Separable potential Green's function matrix element at complex energies a.u. using a hydrogen 1s orbital multiplied by z as a test function versus the number of basis functions

Of particular interest is the complex dynamic polarizability [1]

$$\alpha(E) = -\langle 1s|zG(E+\varepsilon_{1s})z|1s\rangle - \langle 1s|zG(-E+\varepsilon_{1s})z|1s\rangle \tag{43}$$

and the photoionization cross-section given by

$$\sigma(\omega) = \lim_{\eta\to 0^+} (4\pi\omega/c)\,\mathrm{Im}\,\alpha(\omega + i\eta). \tag{44}$$

Only terms corresponding to $l = 1$ contribute to the matrix elements needed here, and we have chosen the following orthonormal radial functions for the separable potential expansion:

$$\omega(j1, r) = [32/(j+1)(j+2)(j+3)(j+4)]^{1/2} r^2 L_j^{(4)}(2r)\exp(-r) \tag{45}$$

We consider first the convergence behaviour of the matrix element $\langle 1s|zG(E)z|1s\rangle$ both on the real axis and in the complex plane. The results, which are plotted versus the number of basis functions in Fig. 2 show relatively fast convergence for both the real and imaginary parts for points far from the real axis. As expected from the estimates given by Eqs. (20) and (21) the convergence becomes slow near the real axis, however.

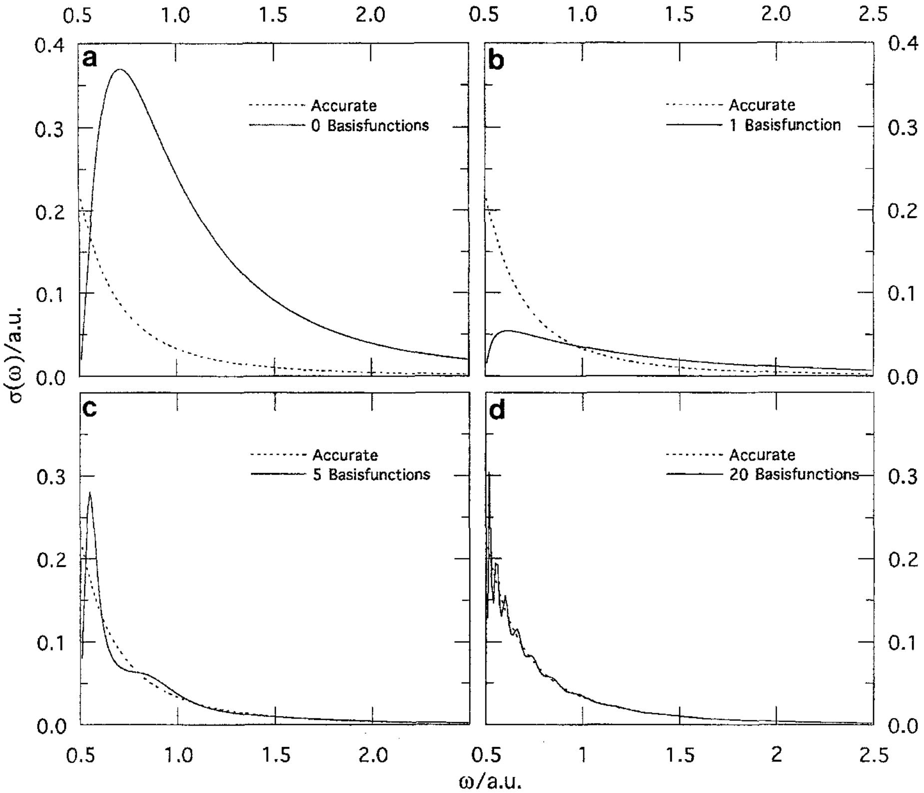

Fig. 3. Separable potential Green's function calculations of the photo-ionization cross section for hydrogen based on 0, 1, 5 and 20 basis functions versus photon energy ω

The separable potential calculations of the photoionization cross-section are compared to the exact curve in Fig. 3. The last term in Eq. (43) does not contribute to $\sigma(\omega)$, and again we evaluate the limit $\eta \to 0^+$ for a fixed number of basis functions. Thus, we have plotted

$$\sigma(\omega) = -(4\pi\omega/c)\,\mathrm{Im}\langle 1s|zG_n(\omega + i0^+ + \varepsilon_{1s})z|1s\rangle \tag{46}$$

for $n = 0, 1, 5$ and 20 versus ω. When ω is larger than about one Hartree just one term in the separable potential suffice to provide a qualitatively acceptable correction to the free particle term and a five term expansion yields essentially the exact result as can be seen from Fig. 2b and c.

In the range 0.5 a.u. $< \omega <$ 1.0 a.u. the situation is more complicated and less satisfactory due to an oscillatory behaviour of the finite rank separable potential calculation of $\sigma(\omega)$. Nevertheless, the present calculation converges toward the exact cross-section whenever $\omega >$ 0.5 a.u.

At the threshold limit, $\omega = 0.5$, approached from above, the density of states of the free particle Green's function is zero. It follows then from Eq. (4) that the separable potential Green's function, $G_n(E)$, will also have a vanishing density of states at this point. Therefore, the calculated photoionization cross-section cannot be non-zero at the threshold and a uniform convergence over the entire energy range is not possible, when the separable potential Green's function construction is based on the free particle Green's function.

A possible solution to this problem might be to replace G_0 in Eq. (4) by a physically more correct Green's function, possibly of the Wentzel–Kramers–Brillouin type for the case of spherical symmetry [1, 12]. Such ideas have been advocated by Linderberg, who gave a reformulation of the many channel scattering problem by using the WKB approximation as the zero order propagator [13]. A more involved solution method for the homogeneous Lippmann–Schwinger equation for potentials having a Coulomb-like long-range behaviour, which uses the full radial Coulomb Green's functions for each angular momentum component as a zero order propagator has recently been developed by Papp [14].

The oscillatory behaviour of the calculated cross-section indicates that the quality of the basis set depends on the energy. It seems plausible to circumvent this unsatisfactory feature by introducing E-dependent basis functions in the separable potential construction as suggested by Adhikari [15]. The convergence analysis given in Sect. 2 shows that the separable potential Green's function would yield the exact matrix element $\langle\phi|G(E)|\phi\rangle$ provided that the function ψ given Eq. (18) could be expanded exactly in the chosen basis $\{\omega_s\}$. We may then conjecture that a fast convergence would result if a chosen basis was augmented either by

$$|\omega_{n+1}\rangle = (-v)^{1/2} G_n(E)|\phi\rangle \tag{47}$$

or a set of E-dependent basis functions designed to have the capability of expanding the right hand side of Eq. (47) accurately. Recent work of Cacelli et al. [16] indicate that simple Slater functions with complex exponents may serve this purpose.

4. Orbital variations generated by variations in a separable potential. Linear response functions

We conclude this paper by providing a tentative outline of a formalism in which variational calculations of bound states and their corresponding response functions are carried out by using the expansion coefficients of a separable potential as the basic variables in the ansatz for a many-electron wave function. The idea of using one-particle potentials as variables to be optimized by using the variation principle has a long history in quantum chemistry [17] and has roots in Slater's ideas on local exchange potentials [18]. In particular, we would like to point out the remarkable work of Talman and Shadwick [19] and Aashamer et al. [20], who optimized local, spherically symmetric potentials for atoms.

For the sake of simplicity we limit ourselves to discuss the approach at the Hartree–Fock and time-dependent Hartree–Fock level. The HF-type calculation is then parametrized through the requirement, that the occupied spin orbitals $\{\phi_l\,|\,l = 1, \dots, N\}$ for an N-electron system should be exact solutions to the eigenvalue equation

$$\{\varepsilon_l + \tfrac{1}{2}\Delta - v_n\}\,\phi_l(x) = 0 \quad (l = 1, 2, \dots, N), \tag{48}$$

where the operator v_n is given by Eq. (1), but it is convenient to adopt a slightly more compact notation. Thus, we shall write the separable potential as a sum of Hermitian terms

$$v(x, x') = \sum v_j(x, x')\,p_j, \tag{49}$$

where each term, v_j, is a member of the set

$$\{\theta_s(x)\theta_s(x')^*;\ \theta_s(x)\theta_{s'}(x')^* + \theta_{s'}(x)\theta_s(x')^*;\ \mathrm{i}(\theta_s(x)\theta_{s'}(x')^* - \theta_{s'}(x)\theta_s(x')^*)\}. \tag{50}$$

Local operators may formally be included above if so desired. Equation (48) implies that the occupied orbitals become functions of the coefficients $\{p_j\}$ implicitly:

$$\phi_l(x) = \phi_l(x;\ p_1 p_2 \ldots). \tag{51}$$

Therefore, also the total energy of the Hartree–Fock state, calculated by using the ordinary many-electron Hamiltonian, will be an implicit function of these parameters,

$$E(p_1 p_2 \ldots) = \langle \mathrm{HF} | \mathrm{H} | \mathrm{HF} \rangle. \tag{52}$$

We do not wish to consider details of the problem of optimizing the energy at present, but we note that those orbital variations, which may cause non-trivial state variations and therefore variations in the energy, are given by

$$|\delta\phi_l\rangle = \lim_{\alpha \to 0^+} G_n(\varepsilon_l + \mathrm{i}\alpha) P v_j |\phi_l\rangle \delta p_j, \tag{53}$$

where the projector onto the complement of the subspace spanned by the occupied orbitals has been introduced

$$P = 1 - \sum_1^N |\phi_l\rangle\langle\phi_l|. \tag{54}$$

Let us assume then that the unperturbed optimization problem has been solved. The optimal parameters of the separable potential will be designated $\{p_j^0\}$. We wish to find an ansatz for time-dependent orbitals in the presence of an adiabatically switched on external perturbation

$$W(t) = \{V \exp(-\mathrm{i}[\omega + \mathrm{i}\eta]t) + V^+ \exp(-\mathrm{i}[-\omega + \mathrm{i}\eta]t)\} \quad (\eta > 0). \tag{55}$$

The external potential will via the optimization procedure induce a time-dependent change in the separable potential, which we write as

$$W_n(t) = \sum v_j(x, x')\{\alpha_j \exp(-\mathrm{i}[\omega + \mathrm{i}\eta]t) + \alpha_j^* \exp(-\mathrm{i}[-\omega + \mathrm{i}\eta]t)\}, \tag{56}$$

where $\{\alpha_j\}$ is a set of variables to be determined from Frenkel's time-dependent variation principle.

Consider now the time-dependent one-particle Schrödinger equation,

$$(\mathrm{i}\, \mathrm{d}/\mathrm{d}t - h_0 - W_n)\Phi_l(t) = 0 \quad (l = 1, 2, \ldots, N), \tag{57}$$

where an unperturbed separable potential Hamiltonian has been defined as

$$h_0 = -\tfrac{1}{2}\Delta + \sum v_j p_j^0. \tag{58}$$

The solution satisfying the initial condition

$$\lim_{t \to -\infty} \Phi_l(t) \exp(\mathrm{i}\varepsilon_l t) = \phi_l \tag{59}$$

may be written through first order as

$$\Phi_l(x, t) = \phi_l(x, t) \exp(-\mathrm{i}\varepsilon_l t), \tag{60}$$

where

$$\phi_l(x,t) = \phi_l(x) + \sum PG_n(\varepsilon_l + \omega + \mathrm{i}\eta)v_j|\phi_l\rangle\alpha_j \exp(-\mathrm{i}[\omega + \mathrm{i}\eta]t)$$
$$+ \sum PG_n(\varepsilon_l - \omega + \mathrm{i}\eta)v_j|\phi_l\rangle\alpha_j^* \exp(-\mathrm{i}[-\omega + \mathrm{i}\eta]t). \tag{61}$$

Strictly speaking the introduction of the projector P here is inconsistent with Eq. (57). It is done for later convenience and, without any loss of generality, in the applications with which we shall be concerned.

As usual in derivations of the time-dependent Hartree–Fock type equations [21], we introduce the following expression for a time-dependent reference state:

$$|\Psi\rangle = \exp(\mathrm{i}\Lambda)|\mathrm{HF}\rangle \exp(-\mathrm{i}\varepsilon), \tag{62}$$

where Λ is a Hermitian, time-dependent one-particle operator satisfying the initial condition

$$\lim_{t\to-\infty} \Lambda(t) = 0 \tag{63}$$

and ε is a real parameter, which shall not concern us here. In a field-theoretic notation we may express the operator Λ as

$$\Lambda = \int \mathrm{d}x\,\mathrm{d}x'\,\psi^+(x)\lambda(x,x')\psi(x'), \tag{64}$$

where $\psi(x)$ denotes the electronic field operator. Let the creation operator corresponding to the occupied, unperturbed spin orbitals $\{\phi_l\}$ be denoted by $\{a_l^+\}$, i.e.

$$a_l^+ = \int \mathrm{d}x\,\psi^+(x)\phi_l(x). \tag{65}$$

We wish to determine the kernel $\lambda(x,x')$ such that the transformed creation operators correspond to the time-dependent spin orbitals given by Eq. (61). Thus, through first order in λ we require that

$$\exp(\mathrm{i}\Lambda)a_l^+\exp(-\mathrm{i}\Lambda) = a_l^+ + \mathrm{i}[\Lambda, a_l^+] + \cdots$$
$$= a_l^+ + \mathrm{i}\int \mathrm{d}x\,\mathrm{d}x'\,\psi^+(x)\lambda(x,x')\phi_l(x') + \cdots$$
$$= \int \mathrm{d}x\,\psi^+(x)\phi_l(x,t) + \cdots, \tag{66}$$

which leads to the following expression:

$$\lambda(x,x') = \sum \{\Delta_j(x,x')\alpha_j \exp(-\mathrm{i}[\omega + \mathrm{i}\eta]t)$$
$$+ \Delta_j^*(x',x)\alpha_j^* \exp(-\mathrm{i}[-\omega + \mathrm{i}\eta]t)\}, \tag{67}$$

where the kernel $\Delta_j(x,x')$ has the ket-bra equivalent

$$\Delta_j = -\mathrm{i}\sum PG_n(\varepsilon_l + \omega + \mathrm{i}\eta)v_j|\phi_l\rangle\langle\phi_l|$$
$$+ \mathrm{i}\sum |\phi_l\rangle\langle\phi_l|v_j G_n(\varepsilon_l - \omega - \mathrm{i}\eta)P. \tag{68}$$

The summation is over $l = 1, 2, \ldots, N$. Using Eqs. (64) and (67) we obtain the following expression for the operator Λ:

$$\Lambda = \sum \{A_j\alpha_j \exp(-\mathrm{i}[\omega + \mathrm{i}\eta]t) + A_j^\dagger\alpha_j^* \exp(-\mathrm{i}[-\omega + \mathrm{i}\eta]t)\}, \tag{69}$$

where a set of frequency-dependent transformation generators have been defined as

$$A_j(\omega + \mathrm{i}\eta) = \int \mathrm{d}x\,\mathrm{d}x'\,\psi^+(x)\Lambda_j(x, x'; \omega + \mathrm{i}\eta)\psi(x'). \tag{70}$$

The adjoint operators satisfy the relation

$$A_j^+(\omega + \mathrm{i}\eta) = A_j(-\omega + \mathrm{i}\eta). \tag{71}$$

In particular, we observe that these generators are Hermitian operators at zero frequency. We are now ready to determine the variables $\{\alpha_j \mid j = 1, 2, \ldots, n^2\}$ from the Frenkel variation principle, which we write as [22]

$$\mathrm{Re}\langle\delta\Psi|\mathrm{i}\,\mathrm{d}/\mathrm{d}t - H - W|\Psi\rangle = 0. \tag{72}$$

This equation leads to a perturbation expansion for the operator Λ only if the generalized Brillouin condition

$$\langle\mathrm{HF}|[A_j(\omega + \mathrm{i}\eta), \mathrm{H}]|\mathrm{HF}\rangle = 0 \tag{73}$$

is satisfied. Contrary to the situation in time-dependent Hartree–Fock and multiconfigurational Hartree–Fock theories the Brillouin condition is not automatically fulfilled, when the unperturbed optimization problem for the ground state representative has been solved. The unperturbed optimization can only ascertain that Eq. (70) is fulfilled at zero frequency. We shall assume here, however, that the unperturbed optimization has been carried out with an accuracy, which for practical purposes amounts to a basis set saturation, and then we have the general Brillouin theorem fulfilled,

$$\langle\mathrm{HF}|[\psi^+(x)\psi(x'), \mathrm{H}]|\mathrm{HF}\rangle = 0. \tag{74}$$

Equation (73) follows from Eq. (74) since A_j is a one-particle operator.

A first order equation for the operator Λ follows from the Frenkel variation principle as

$$\mathrm{i}\langle\mathrm{HF}|[\delta\Lambda, \partial\Lambda/\partial t]|\mathrm{HF}\rangle - \langle\mathrm{HF}|[[\delta\Lambda, \mathrm{H}], \Lambda]|\mathrm{HF}\rangle + \mathrm{i}\langle\mathrm{HF}|[\delta\Lambda, \mathrm{W}]|\mathrm{HF}\rangle = 0, \tag{75}$$

where

$$\delta\Lambda = \sum \{A_j\,\delta\alpha_j \exp(-\mathrm{i}[\omega + \mathrm{i}\eta]t) + A_j^+\,\delta\alpha_j^* \exp(-\mathrm{i}[-\omega + \mathrm{i}\eta]t)\}. \tag{76}$$

When Eqs. (76) and (69) are introduced into Eq. (75) the following time-dependent factors will occur:

$$\exp(-\mathrm{i}2[\omega + \mathrm{i}\eta]t), \quad \exp(2\eta t) \text{ and } \exp(-\mathrm{i}2[-\omega + \mathrm{i}\eta]t). \tag{77}$$

Of these the first and the last are oscillatory. They will be omitted on the grounds that their time average vanish in the limit $\eta = 0$. Furthermore, their coefficients as they appear in Eq. (75) vanish identically in the limit of completely arbitrary potential variations just as similar terms in the derivation of the ordinary time-dependent Hartree–Fock equations. Then Eq. (75) reduces to a linear system of equations for the variables $\{\alpha_j\}$:

$$\begin{aligned}&\sum \{\langle\mathrm{HF}|[A_j^+, A_{j'}]|\mathrm{HF}\rangle(\omega + \mathrm{i}\eta) - \langle\mathrm{HF}|[[A_j^+, \mathrm{H}], A_{j'}]|\mathrm{HF}\rangle\}\alpha_{j'}\\ &\quad = -\mathrm{i}\langle\mathrm{HF}|[A_j^+, \mathrm{V}]|\mathrm{HF}\rangle.\end{aligned} \tag{78}$$

Linear response functions are finally derived from the time-dependent expectation value of a general operator

$$\langle \Psi | R | \Psi \rangle = \langle \mathrm{HF} | R | \mathrm{HF} \rangle + \langle\langle R; V \rangle\rangle_{\omega + i\eta} \exp(-i[\omega + i\eta]t) + \langle\langle R; V^{+} \rangle\rangle_{-\omega + i\eta} \exp(-i[-\omega + i\eta]t), \tag{79}$$

with the result that

$$\langle\langle R^{+}; V \rangle\rangle_{\omega + i\eta} = (R|A)\{(A|A)(\omega + i\eta) - (A|H|A)\}^{-1}(A|V) \tag{80}$$

in a super operator notation [23]. We employ here the following definitions:

$$(X|Y) = \langle \mathrm{HF} | [X^{+}, Y] | \mathrm{HF} \rangle \tag{81}$$

and

$$(X|H|Y) = \langle \mathrm{HF} | [X^{+}, [H, Y]] | \mathrm{HF} \rangle. \tag{82}$$

The compact response function formula given by Eq. (80) is similar to well-established expressions [24]. It derives from a much more involved and frequency dependent set of transformation generators $\{A_j(\omega + i\eta)\}$, but it has the gratifying feature that the effects of the continuum of one-particle states is included in a closed form.

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