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Convergence of partial-wave expansions for energies, scattering amplitudes and positron annihilation rates

G F Gribakin and J Ludlow

Department of Applied Mathematics and Theoretical Physics, The Queen's University of Belfast, Belfast BT7 1NN, UK

E-mail: g.gribakin@am.qub.ac.uk and j.ludlow@am.qub.ac.uk

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Abstract

We use many-body theory to find the asymptotic behaviour of second-order correlation corrections to the energies and positron annihilation rates in many-electron systems with respect to the angular momenta l of the single-particle orbitals included. The energy corrections decrease as $1/(l+\frac{1}{2})^4$, in agreement with the result of Schwartz, whereas the positron annihilation rate has a slower $1/(l+\frac{1}{2})^2$ convergence rate. We illustrate these results by numerical calculations of the energies of Ne and Kr and by examining results from extensive configuration-interaction calculations of PsH binding and annihilation.

1. Introduction

Calculations of atomic properties usually begin with a central-field approximation (e.g. Hartree–Fock), which enables one to generate a set of single-particle orbitals of the ground and excited atomic states. These orbitals are characterized by their angular momenta (s, p, d, etc). They can then be used to go beyond the mean-field approximation and include correlation effects. This can be done in various ways, e.g. through a configuration-interaction (CI) expansion of the total wavefunction, or by using many-body perturbation theory to evaluate the second-order and higher corrections to the quantities of interest. In doing so it is important to achieve convergence with respect to the number of different angular momenta (partial waves), as well as the number of single-particle orbitals in each partial wave included in the CI expansion or perturbation-theory sums.

A major difficulty here is to account for the continuous spectrum of the energies. There are a number of basis sets that replace the continuum by a discrete set of states which is effectively complete. Some common examples are Laguerre, B-spline and Gaussian bases (see, e.g., Bray and Stelbovics 1992, Sapirstein and Johnson 1996, Moncrieff and Wilson 1999, respectively). However, there is still a question of convergence with respect to the angular momentum of the single-particle orbitals included. This question was first studied in a seminal work by Schwartz (1962). He showed that the contribution of the electron orbitals with the angular

momentum l to the second-order correction to the ground state energy of a two-electron atom drops as $\Delta E_2^{(l)} \simeq -(45/256)(l+\frac{1}{2})^{-4} + \mathrm{O}((l+\frac{1}{2})^{-6})$, if one starts from the independent-electron (hydrogen-like) approximation. The problem was later investigated in a number of works both analytically and numerically (Byron and Joachain 1967, Carroll and Silverstone 1979, Schmidt and Hirschhausen 1983, Hill 1985, Salomonson and Öster 1989, Kutzelnigg and Morgan 1992). In particular, they looked at convergence of angular-momentum expansions for excited two-electron states, and in nonperturbative CI calculations.

In this work we generalize the above result to obtain an analytic expression for the asymptotic behaviour of the second-order energy correlation correction to the Hartree–Fock ground state of a closed-shell atom. Using atomic many-body theory we also obtain the asymptotic formulae for the correlation corrections to the single-particle energies and scattering amplitudes in many-electron atoms, and investigate the convergence of the positron–atom annihilation rates. The latter shows a slower $(l+\frac{1}{2})^{-2}$ decrease.

We use a B-spline Hartree–Fock basis set to check the validity of our results numerically. We also use the data of Mitroy *et al* (2001) to investigate the difference in the convergence rate of the energy and annihilation rate of a system containing positrons, PsH.

2. Asymptotic formula for the total energy

Our derivation of the asymptotic formula for the second-order correction to the energy of a many-electron atom is based on the method of Schwartz (1962, 1963). To make this development more transparent, let us first show how the calculation is done for a He-like $1s^2$ system.

2.1. Ground state two-electron atoms

For a two-electron atom or ion with nuclear charge Z, one can treat the Coulomb repulsion between the electrons as a perturbation, and thus obtain the well known expansion for the ground state energy (e.g. Landau and Lifshitz 1977)

$$E = -Z^2 + \tfrac{5}{8}Z + \Delta E_2 + \cdots, \tag{1}$$

where

$$\Delta E_2 = \sum_{\alpha,\beta} \frac{|\langle \alpha,\beta|V|1s,1s\rangle|^2}{2\varepsilon_{1s} - \varepsilon_\alpha - \varepsilon_\beta} \tag{2}$$

is the second-order correction to the energy (we use atomic units). The sum above includes all excited states and α and β are the hydrogen-like states nlm with energies ε_α and ε_β (n here describes both discrete and continuous spectrum orbitals). If the Coulomb interaction $V = 1/r_{12}$ is expanded in terms of Legendre polynomials

$$V = \sum_{l=0}^{\infty} V^{(l)} \equiv \sum_{l=0}^{\infty} P_l(\cos\theta)\frac{r_<^l}{r_>^{l+1}}, \tag{3}$$

where $r_< = \min(r_1, r_2)$, $r_> = \max(r_1, r_2)$, its lth term describes the contribution of the excited states with orbital angular momentum l to (2), $\Delta E_2^{(l)}$.

The second-order correction ΔE_2 can also be expressed in the form

$$\Delta E_2 = \langle \psi_0 | V | \psi_1 \rangle, \tag{4}$$

where

$$|\psi_1\rangle = \sum_{\alpha,\beta} \frac{|\alpha,\beta\rangle\langle\alpha,\beta|V|1s,1s\rangle}{E_0 - \varepsilon_\alpha - \varepsilon_\beta}, \tag{5}$$

$|\psi_0\rangle \equiv |1s, 1s\rangle$, and $E_0 \equiv 2\varepsilon_{1s}$. In the coordinate representation ψ_1 satisfies the equation

$$(E_0 - H_0)\psi_1 = (1/r_{12} - E_1)\psi_0, \tag{6}$$

where

$$H_0 = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 - \frac{Z}{r_1} - \frac{Z}{r_2} \tag{7}$$

is the first-order correction to the ground state wavefunction, $\psi_0 = R_{1s}(r_1)R_{1s}(r_2)/4\pi$ is the $1s^2$ wavefunction in coordinate form and $E_1 = \langle\psi_0|V|\psi_0\rangle = 5Z/8$.

Deriving an asymptotic formula for

$$\Delta E_2^{(l)} = \langle\psi_0|V^{(l)}|\psi_1\rangle \tag{8}$$

we are interested in the behaviour of ψ_1 in the limit of high l. As seen from equation (3), for large l the Coulomb interaction is strongly peaked at $r_1 \approx r_2$. Therefore, we need to evaluate ψ_1 in the region of space where $\boldsymbol{r}_1 \approx \boldsymbol{r}_2$. This region is dominated by the singularity of the $1/r_{12}$ term on the right-hand side of equation (6), and the only significant terms in (6) are those that depend on the inter-electron distance r_{12}. It is therefore natural to change to the centre-of-mass and relative coordinates defined by

$$\boldsymbol{R} = (\boldsymbol{r}_1 + \boldsymbol{r}_2)/2, \qquad \boldsymbol{r}_{12} = \boldsymbol{r}_1 - \boldsymbol{r}_2. \tag{9}$$

Transforming equation (6) to the new coordinates and keeping only those terms that depend on r_{12} we obtain

$$\frac{1}{2\mu}\Delta_{12}\psi_1 \simeq \frac{\psi_0}{r_{12}}, \tag{10}$$

where $\mu = 1/2$ is the reduced mass of the two electrons. This equation may be integrated easily using the spherical polar form of the Laplacian[1] to yield

$$\psi_1 = (r_{12}/2)\psi_0. \tag{11}$$

To calculate $\Delta E_2^{(l)}$, ψ_1 may be expanded in partial waves by using the expansion of r_{12} (Varshalovich *et al* 1988)

$$r_{12} = \sum_{l=0}^{\infty} r_{12}^{(l)} = \sum_{l=0}^{\infty} P_l(\cos\theta)\frac{r_<^l}{r_>^{l+1}}\left(\frac{r_<^2}{2l+3} - \frac{r_>^2}{2l-1}\right). \tag{12}$$

To calculate the integral over $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ in equation (8), it is convenient to introduce new variables r and σ,

$$r_1 = r(1-\sigma), \qquad r_2 = r(1+\sigma), \tag{13}$$

$$r_< = r(1-|\sigma|), \qquad r_> = r(1+|\sigma|). \tag{14}$$

Since $r_1 \approx r_2$ gives the dominant contribution to the integral, it can be assumed that σ is small, $|\sigma| \ll 1$. Using the Jacobian

$$\begin{vmatrix} \partial r_1/\partial r & \partial r_1/\partial\sigma \\ \partial r_2/\partial r & \partial r_2/\partial\sigma \end{vmatrix} = 2r \tag{15}$$

we obtain for the integration volume element

$$r_1^2\,\mathrm{d}r_1\,r_2^2\,\mathrm{d}r_2\,\mathrm{d}\Omega_1\,\mathrm{d}\Omega_2 = 2r^5(1-\sigma^2)^2\,\mathrm{d}r\,\mathrm{d}\sigma\,\mathrm{d}\Omega_1\,\mathrm{d}\Omega_2, \tag{16}$$

where the term in σ^2 can be neglected (see below).

[1] For small r_{12} the function ψ_0 can be regarded as constant.

The leading term of the lth spherical component of r_{12} in powers of $l+\frac{1}{2}$ is

$$\frac{r_<^l}{r_>^{l+1}}\left(\frac{r_<^2}{2l+3}-\frac{r_>^2}{2l-1}\right)=-r\frac{(1-|\sigma|)^l}{(1+|\sigma|)^{l+1}}\frac{1+2|\sigma|(l+\frac{1}{2})}{(l+\frac{1}{2})^2}[1+\mathrm{O}(l^{-2})], \quad (17)$$

and the lth component of the Coulomb potential is

$$\frac{r_<^l}{r_>^{l+1}}=\frac{1}{r}\frac{(1-|\sigma|)^l}{(1+|\sigma|)^{l+1}}. \quad (18)$$

Integration over σ can be simplified by using the expansion

$$\left(\frac{1-x}{1+x}\right)^l=\exp[-2lx(1+x^2/3+x^4/5+\cdots)]=\mathrm{e}^{-2lx}[1+\mathrm{O}(lx^3)], \quad (19)$$

leading to

$$\frac{(1-|\sigma|)^l}{(1+|\sigma|)^{l+1}}\simeq\mathrm{e}^{-2(l+1/2)|\sigma|}[1+\mathrm{O}(l^{-2})]. \quad (20)$$

The form of the exponent shows that $|\sigma|\sim l^{-1}\ll 1$ will dominate the integral. We have used this fact above to estimate the error term. Accordingly, the ground state wavefunction can be expanded about $r_1=r_2$

$$\psi_0(\boldsymbol{r}_1,\boldsymbol{r}_2)=R_{1\mathrm{s}}(r)R_{1\mathrm{s}}(r)/(4\pi)+\mathrm{O}(\sigma^2). \quad (21)$$

Equations (16)–(18), (20) and (21) can be used to write equation (8) as

$$\Delta E_2^{(l)}\simeq-\int\frac{R_{1\mathrm{s}}^4(r)}{(4\pi)^2}\frac{1+2|\sigma|(l+\frac{1}{2})}{(l+\frac{1}{2})^2}\mathrm{e}^{-4(l+1/2)|\sigma|}P_l^2(\cos\theta)r^5\,\mathrm{d}r\,\mathrm{d}\sigma\,\mathrm{d}\Omega_1\,\mathrm{d}\Omega_2. \quad (22)$$

In this form we have neglected all higher-order terms, like $\mathrm{O}(\sigma^2)$ and $\mathrm{O}(l^{-2})$ and beyond.

The angular part of the above integral gives

$$\int P_l^2(\cos\theta)\,\mathrm{d}\Omega_1\,\mathrm{d}\Omega_2=\frac{16\pi^2}{2l+1}. \quad (23)$$

The integration over σ can be formally extended from $-\infty$ to $+\infty$, because for large l the integrand decreases exponentially beyond $|\sigma|\sim l^{-1}$, which yields

$$\int_{-\infty}^{+\infty}\mathrm{e}^{-4(l+1/2)|\sigma|}[1+2|\sigma|(l+1/2)]\,\mathrm{d}\sigma=\frac{3}{8}\frac{1}{(l+\frac{1}{2})}. \quad (24)$$

Finally, the asymptotic form of the second-order correction to the ground state energy of the two-electron atom for large angular momenta l of the single-particle orbitals included is

$$\Delta E_2^{(l)}=-\frac{3}{8}\frac{1}{(l+\frac{1}{2})^4}\int_0^\infty R_{1\mathrm{s}}^4(r)r^5\,\mathrm{d}r+\mathrm{O}\left(\frac{1}{(l+\frac{1}{2})^6}\right). \quad (25)$$

The l^{-6} dependence of the error is due to the fact that only terms with additional factors of order σ^2 or l^{-2} and higher have been neglected.

For the hydrogen-like zeroth approximation, $R_{1\mathrm{s}}=2Z^{3/2}\mathrm{e}^{-Zr}$, the integral over r can be evaluated analytically, and we get

$$\Delta E_2^{(l)}\simeq-\frac{45}{256(l+\frac{1}{2})^4}+\mathrm{O}\left(\frac{1}{(l+\frac{1}{2})^6}\right) \quad (26)$$

in exact agreement with Schwartz's result. Note, however, that equation (25) enables one to find the constant C in the asymptotic behaviour of the second-order correction, $\Delta E_2^{(l)}\simeq -C/(l+\frac{1}{2})^4$, numerically in other cases, e.g. when one starts from the Hartree–Fock approximation.

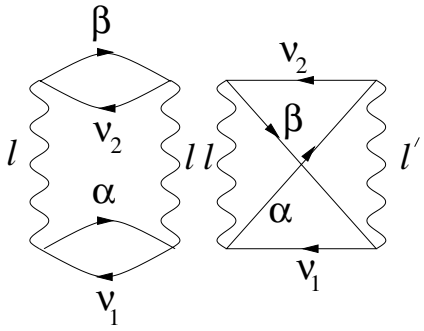

Figure 1. Diagrammatic representation of the second-order perturbation theory correction to the ground state energy of a closed-shell atom. The indices l and l' represent the angular momentum transferred through the Coulomb interaction.

2.2. Extension to closed-shell atoms

The formalism developed to treat two-electron atoms can be simply extended to treat more complex closed-shell atoms. Instead of a hydrogen-like model the calculation of a many-electron atom usually starts with the Hartree–Fock approximation. In this case each electron moves independently in a self-consistent central field created by the nucleus and the other electrons. Hence, there is no first-order correction to the ground state energy due to the interelectron Coulomb interaction. Otherwise, the situation is very similar to that treated above. The second-order perturbation theory correction can be represented by the diagrams in figure 1.

Analytically, it corresponds to the following sum of the direct and exchange contributions (see, e.g., Lindgren and Morrison 1982):

$$\Delta E_2 = \frac{1}{2}\sum_{\substack{\alpha,\beta\\ \nu_1,\nu_2}} \left(\frac{4|\langle \alpha, \beta|V|\nu_1, \nu_2\rangle|^2}{\varepsilon_{\nu_1} + \varepsilon_{\nu_2} - \varepsilon_\alpha - \varepsilon_\beta} - \frac{2\langle \nu_2, \nu_1|V|\alpha, \beta\rangle\langle \alpha, \beta|V|\nu_1, \nu_2\rangle}{\varepsilon_{\nu_1} + \varepsilon_{\nu_2} - \varepsilon_\alpha - \varepsilon_\beta} \right) \tag{27}$$

where the sum over $\nu_1 \equiv n_1 l_1 m_1$ and $\nu_2 \equiv n_2 l_2 m_2$ includes all occupied single-electron states ('holes'), and that over α and β runs over all excited states ('particles'). Together they form a complete set of eigenstates of the Hartree–Fock Hamiltonian of the ground state atom. The factors 4 and 2 in the brackets appear as a result of summation over the electron spins.

For fixed ν_1 and ν_2 the first term in equation (27) is similar to the second-order correction (2). Hence, it can be treated in a way similar to that outlined in equations (4)–(11), provided we use

$$\psi_0 = R_{n_1 l_1}(r_1) R_{n_2 l_2}(r_2) Y_{l_1 m_1}(\hat{\boldsymbol{r}}_1) Y_{l_2 m_2}(\hat{\boldsymbol{r}}_2) \tag{28}$$

and replace H_0 with the Hartree–Fock Hamiltonian of [2] electrons 1 and 2. We also apply the same procedure to the exchange term in equation (27).

As a result, the contribution of the angular momentum l to the second-order energy correction can be written as

$$\Delta E_2^{(l)} = \sum_{\nu_1,\nu_2} \left(2\langle \psi_0|V^{(l)}|\psi_1^{(l)}\rangle - \sum_{l'} \langle \tilde{\psi}_0|V^{(l')}|\psi_1^{(l)}\rangle \right), \tag{29}$$

[2] In this case the $V_1\psi_0$ term on the right-hand side of equation (6) is replaced by a sum over all occupied states $\sum_{\nu_3,\nu_4} |\nu_3, \nu_4\rangle\langle \nu_3, \nu_4|V|\nu_1, \nu_2\rangle$. However, this term is nonsingular at $r_{12} \to 0$ and equation (10) remains valid.

where $\psi_1^{(l)} = \frac{1}{2} r_{12}^{(l)} \psi_0$ and $\tilde{\psi}_0$ is the function (28) with the coordinates of the first and second electrons switched. The sum runs over all ground state subshells $n_1 l_1$, $n_2 l_2$, as well as the magnetic quantum numbers m_1 and m_2 within each subshell.

As before we transform the radial coordinates r_1 and r_2 to r and σ and apply equations (17)–(20). The function ψ_0 is then expanded as (cf (21))

$$\psi_0(\boldsymbol{r}_1, \boldsymbol{r}_2) = R_{n_1 l_1}(r) R_{n_2 l_2}(r) Y_{l_1 m_1}(\hat{\boldsymbol{r}}_1) Y_{l_2 m_2}(\hat{\boldsymbol{r}}_2) + \mathrm{O}(\sigma). \tag{30}$$

The radial integrals over r and σ in the direct and exchange matrix elements in equation (29) are identical and can be factored out of the sum over m_1 and m_2. They give

$$-\frac{3}{8(l+\frac{1}{2})^3} \int_0^\infty R_{n_1 l_1}^2(r) R_{n_2 l_2}^2(r) r^5 \, \mathrm{d}r \left[1 + \mathrm{O}\left(\frac{1}{(l+\frac{1}{2})^2} \right) \right]. \tag{31}$$

Note unlike (21), expansion (30) contains terms linear in σ. However, they do not give rise to $1/(l+1/2)$ corrections. Their contribution to the integral is zero because the rest of the integrand is an even function of σ.

The angular part of the direct term in (29) is

$$\sum_{m_1, m_2} \int Y_{l_1 m_1}^*(\hat{\boldsymbol{r}}_1) Y_{l_2 m_2}^*(\hat{\boldsymbol{r}}_2) P_l^2(\cos\theta) Y_{l_1 m_1}(\hat{\boldsymbol{r}}_1) Y_{l_2 m_2}(\hat{\boldsymbol{r}}_2) \, \mathrm{d}\Omega_1 \, \mathrm{d}\Omega_2 = \frac{(2l_1+1)(2l_2+1)}{2(l+\frac{1}{2})}, \tag{32}$$

where we use $\sum_{m_1} Y_{l_1 m_1}^*(\hat{\boldsymbol{r}}_1) Y_{l_1 m_1}(\hat{\boldsymbol{r}}_1) = (2l_1+1)/4\pi$ (Varshalovich *et al* 1988). The angular integral of the exchange contribution is of the form

$$\sum_{l'} \sum_{m_1, m_2} \int Y_{l_1 m_1}^*(\hat{\boldsymbol{r}}_2) Y_{l_2 m_2}^*(\hat{\boldsymbol{r}}_1) P_l(\cos\theta) P_{l'}(\cos\theta) Y_{l_1 m_1}(\hat{\boldsymbol{r}}_1) Y_{l_2 m_2}(\hat{\boldsymbol{r}}_2) \, \mathrm{d}\Omega_1 \, \mathrm{d}\Omega_2. \tag{33}$$

This sum is reduced to an integral involving four spherical harmonics, which is calculated in a standard way (Varshalovich *et al* 1988) and gives

$$(2l_1+1)(2l_2+1) \sum_{l', L} (2L+1) \begin{pmatrix} L & l & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}^2, \tag{34}$$

where L is an auxiliary summation variable. Its range is limited by the triangular condition $|l_1 - l_2| \leqslant L \leqslant l_1 + l_2$. Since l_1 and l_2 are the angular momenta of some ground state orbitals (s, p, d or at most f), their values are small, $l_{1,2} \sim 1$, hence $L \sim 1$. Therefore, in the large-l limit only $l' \approx l$ give a nonzero contribution to the sum over l' in (34). Asymptotically, we have

$$\sum_{l'} \begin{pmatrix} L & l & l' \\ 0 & 0 & 0 \end{pmatrix}^2 \simeq \sum_{l'} \frac{2l'+1}{2l+1} \begin{pmatrix} L & l & l' \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{1}{2l+1} \qquad (l \gg 1), \tag{35}$$

the relative error in this formula being of order l^{-2} (Kutzelnigg and Morgan 1992). Equation (34) thus becomes

$$\frac{(2l_1+1)(2l_2+1)}{2l+1} \sum_{L} (2L+1) \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{(2l_1+1)(2l_2+1)}{2(l+\frac{1}{2})}, \tag{36}$$

which is exactly the same as equation (32). The direct contribution in equation (29) comes with an extra spin factor of 2. We therefore see that in the limit of high l the exchange term cancels exactly half of the direct term.

Combining equations (31), (32) and (36), we obtain the asymptotic contribution of the ground state orbitals n_1l_1, n_2l_2 at high transferred angular momenta l as

$$\Delta E_2^{(l)}(n_1l_1, n_2l_2) = -\frac{C_{n_1l_1n_2l_2}}{(l+\frac{1}{2})^4} + \mathrm{O}\left(\frac{1}{(l+\frac{1}{2})^6}\right), \tag{37}$$

where

$$C_{n_1l_1n_2l_2} = \tfrac{3}{8}(2l_1+1)(2l_2+1)\int_0^\infty R^2_{n_1l_1}(r)R^2_{n_2l_2}(r)r^5\,\mathrm{d}r. \tag{38}$$

Its size is proportional to a specific overlap integral of the densities, and to the numbers of electrons in these orbitals, as given by the $(2l_1+1)(2l_2+1)$ factor. For $n_1l_1 = n_2l_2 = 1\mathrm{s}$ we recover the original result (25).

Accordingly, the total second-order correction

$$\Delta E_2^{(l)} = -\frac{C}{(l+\frac{1}{2})^4} + \mathrm{O}\left(\frac{1}{(l+\frac{1}{2})^6}\right) \tag{39}$$

is determined by the sum over all ground state orbitals n_1l_1, n_2l_2,

$$C = \sum_{n_1l_1,n_2l_2} C_{n_1l_1n_2l_2}. \tag{40}$$

There is an important distinction between this result and that obtained for a He-like $1\mathrm{s}^2$ atom. Here l is the angular momentum transferred along the Coulomb interaction, which may be different from the angular momentum of the excited single-particle orbitals included in the perturbation-theory sum. For ground state orbitals $l_{1,2} \neq 0$, the angular momenta of the excited states α and β obey the triangular condition, e.g. $|l - l_1| \leqslant l_\alpha \leqslant l + l_1$, which means that asymptotically, for $l \gg 1$, one has $l_{\alpha,\beta} \approx l$. Therefore, if one examines the behaviour of ΔE_2 as a function of $l_{\max} = \max(l_\alpha, l_\beta)$, rather than l, the contributions of successively larger $l_{\max}$ will drop as $(l_{\max}+\frac{1}{2})^{-4}$. However, the next term may now be of order $(l_{\max}+\frac{1}{2})^{-5}$, rather than $(l+\frac{1}{2})^{-6}$, as in equation (39).

In nonperturbative CI calculations the contribution of configurations which include high-angular-momentum orbitals is always small, and thus perturbative. Therefore, it is natural that asymptotically the increments of the total energy due to the inclusion of such states drop as $(l+\frac{1}{2})^{-4}$, the next term being of order $(l+\frac{1}{2})^{-5}$. The asymptotic constant C no longer has the form of (38), but depends on the total wavefunction, e.g. for a He-like ground state

$$C = 6\pi^2 \int |\Psi(\boldsymbol{r}, \boldsymbol{r})|^2 r^5\,\mathrm{d}r, \tag{41}$$

where $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the exact wavefunction (Hill 1985).

3. Numerical calculations

In this section we compare the results of a direct numerical calculation of the perturbation theory sums (27) for a range of transferred angular momenta l with the asymptotic behaviour of the second-order energy correction, equations (37)–(40). The purpose of this comparison is twofold. Firstly, it tests the asymptotic formulae numerically and shows how quickly $\Delta E_2^{(l)}$ converges to them. Secondly, it tests the effective completeness of our single-electron basis set for a wide range of angular momenta.

We started from a standard Hartree–Fock calculation of the atomic ground state, and then solved the Hartree–Fock equations for excited orbitals using B-splines (De Boor 1978, Sapirstein and Johnson 1996). In this work $n = 90$ B-splines of order $k = 10$ are used with a

cavity radius of $R = 20$ au. The radial knot set $\{t_i\}$ was chosen so as to match the exponential behaviour of the atomic wavefunctions

$$t_1 = t_2 = \cdots = t_k = 0, \tag{42}$$

$$t_{n+1} = t_{n+2} = \cdots = t_{n+k} = R, \tag{43}$$

$$t_i = r_0[\mathrm{e}^{\beta(i-k)} - 1] \qquad (i = k+1, \ldots, n), \tag{44}$$

where

$$\beta = \frac{\ln(R/r_0 + 1)}{(n + 1 - k)}, \tag{45}$$

and $r_0 = 10^{-3}$ was chosen. This knot sequence ensured that we had enough splines to describe the rapid variation of the wavefunctions at small distances and large energies[3].

By expanding the Hartree–Fock wavefunctions in terms of the B-splines, the Hartree–Fock equations were reduced to a generalized eigenvalue problem solved using standard routines (Sapirstein and Johnson 1996). This provided a set of single-particle orbitals with angular momenta between 0 and 30, which we used to calculate the contributions of various pairs of hole states and transferred angular momenta l to (27).

To test the validity of the asymptotic formula, a number of noble gas atoms were examined. Figure 2 shows the asymptotic convergence of the second-order energy with respect to l, for various pairs of ground state orbitals in Ne.

The graphs show that in agreement with equation (37) the quantities $-\Delta E_2^{(l)}(n_1 l_1, n_2 l_2)$ $(l + \frac{1}{2})^4$ do converge towards their asymptotic values $C_{n_1 l_1 n_2 l_2}$. However, all the graphs show a loss of accuracy at high values of $l \gtrsim 15$ due to numerical difficulties in dealing with the cusp in the inter-electron Coulomb interaction. Therefore, for high angular momenta the effective 'completeness' of our excited-state basis set deteriorates, as far as the calculation of $\Delta E_2^{(l)}$ is concerned.

This feature is easy to understand. As we have seen in section 2, at high l the function $\psi_1^{(l)}$ has a very narrow cusp at $r_1 = r_2$, which gives a leading contribution to $\Delta E_2^{(l)}$. Equations (14) and (20) show that its width is $\Delta r \sim r/l$. In the direct calculation of the perturbation-theory sum this cusp is implicitly constructed from the excited-state orbitals (cf equation (5)) based on the B-spline knot sequence (44). Therefore, the 'completeness' holds only as long as the knot sequence interval $\Delta r \simeq \beta r$ is smaller than the width of the cusp, which is equivalent to

$$l \lesssim 1/\beta. \tag{46}$$

Numerically this gives $l \lesssim 10$ for the set of splines defined above ($\beta = 0.109$).

Condition (46) means that the quality of the excited state basis is uniform for all radii. Narrowing of the Coulomb cusps at small r is matched by the smaller intervals of the B-spline radial knot sequence (44). This property is a consequence of the exponential knot sequence, and can serve as an argument in favour of such choice. It is illustrated by figure 2, where the loss of accuracy is similar for the inner 1s and outer 2p orbitals, although they have very different radii.

To further illustrate condition (46) we have performed another calculation of the second-order energies of Ne, using a smaller set of $n = 40$ B-splines of order $k = 6$ and a larger radius $R = 40$ au. The corresponding $\beta = 0.303$ means that the excited state sets are complete for $l \lesssim 3$. Indeed, the error in the numerical values of $\Delta E_2^{(l)}$ grows rapidly for $l > 5$, see figures 1(a) and (d).

[3] An exponential knot sequence in coordinate space generates a set of quasicontinuum orbitals with exponentially increasing energies, $\varepsilon_n \sim \varepsilon_0 \mathrm{e}^{\gamma n}$, which is in some sense optimal for spanning the continuum.

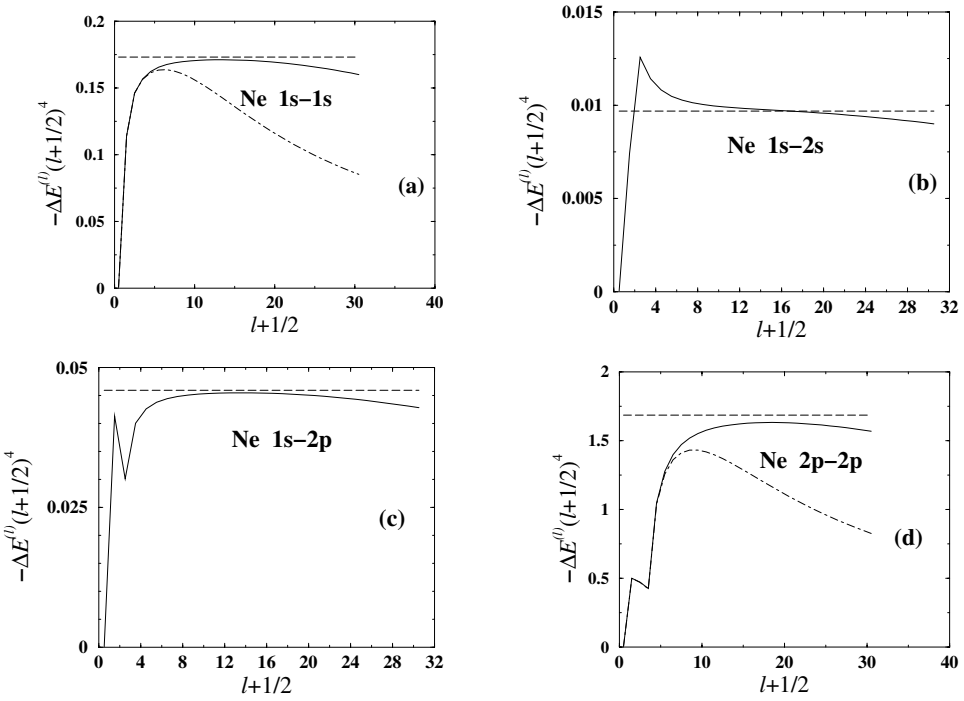

Figure 2. Test of the convergence of the second-order energies for various pairs of ground state orbitals in Ne to their asymptotic form. Solid curves are the contributions of particular pairs of hole states to the second-order correction, $\Delta E_2^{(l)}(n_1l_1, n_2l_2)$ times $(l + \frac{1}{2})^4$. Horizontal dashed curves show the asymptotic constants $C_{n_1l_1n_2l_2}$, as given by equation (38): (*a*) 1s–1s, $C_{1s1s} = 0.173\,114$; (*b*) 1s–2s, $C_{1s2s} = 0.009\,682$; (*c*) 1s–2p, $C_{1s2p} = 0.045\,933$; (*d*) 2p–2p, $C_{2p2p} = 1.684\,838$. Chain curves in (*a*) and (*d*) show the second-order energy calculated with $n = 40$ B-splines of order $k = 6$, using $R = 40$ au.

Table 1. Contributions of different orbitals to the second-order correction to the ground state energy of Ne obtained using $n = 90$ splines of order $k = 10$, $R = 20$ au.

Pair	ΔE_2 [a] (au)	$C_{n_1l_1n_2l_2}$ [b]	ΔE_2 [c] (au)	ΔE_2 [d] (au)
1s–1s	−0.040 213	0.173 114	−0.040 256	−0.040 255
1s–2s	−0.005 553	0.009 682	−0.005 558	−0.005 557
2s–2s	−0.011 981	0.235 741	−0.012 040	−0.012 037
1s–2p	−0.022 071	0.045 933	−0.022 094	−0.022 094
2s–2p	−0.086 895	0.617 663	−0.087 203	−0.087 188
2p–2p	−0.220 578	1.684 838	−0.220 998	−0.220 973

[a] Summed up to $l = 10$.
[b] Asymptotic constants, equation (38).
[c] Obtained by extrapolating $l > 10$ values using equation (37).
[d] Extrapolated results by Flores (1992).

Therefore, it may be more accurate to truncate the partial wave expansion of the second-order energy at a lower value of l and then correct the result using the asymptotic formula. Table 1 shows the values of $\Delta E_2^{(l)}$ for different pairs of orbitals of Ne obtained by truncating the partial wave expansions at $l = 10$ and then using equation (37) to extrapolate the results. As can be seen the results agree closely with those of Flores (1992).

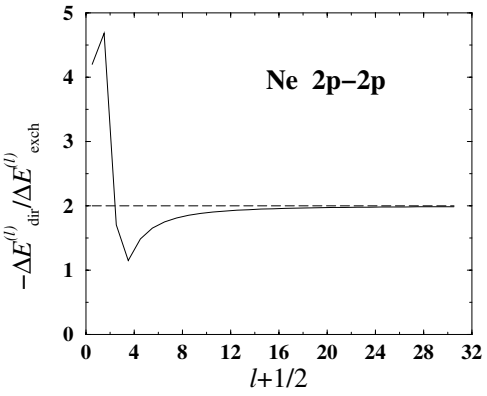

Figure 3. Ratio of the direct to exchange contribution to the second-order energy of Ne for the 2p–2p pair. ——, numerical; — — —, asymptotic ratio.

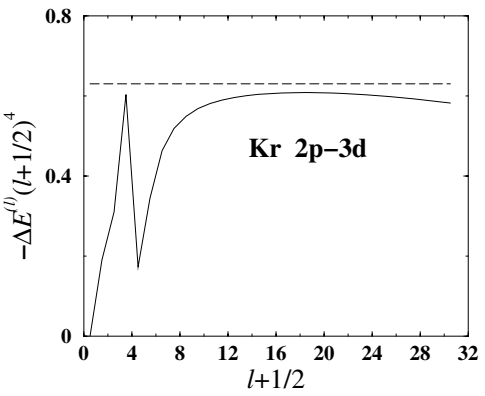

Figure 4. Test of the asymptotic formula for the second-order correction to the 2p–3d energy in Kr: ——, numerical; — — —, asymptotic value $C_{\rm 2p3d} = 0.630\,29$.

It is of interest to ascertain whether the exchange contribution does cancel half of the direct contribution in the limit of high l as theory predicts. Figure 3 shows that the ratio beteen the direct and exchange terms does indeed tend to -2, in agreement with theory.

An interesting feature of $\Delta E_2^{(l)}$ is its nonmonotonic approach to the limit value. Some of the graphs in figure 2 show a strong dip at low values of l. This feature is even stronger in other cases, for example for the second-order 2p–3d energy correction in Kr, figure 4.

This is due to a large contribution from the exchange diagram. In general, Coulomb matrix elements are smaller for larger values of the transferred angular momentum. For holes with nonzero angular momentum the value of l' in the exchange diagram (figure 1) can be *lower* than l. If l is not high, the Coulomb matrix element of $V^{(l')}$ can be considerably greater than that of $V^{(l)}$, which favours the exchange contribution. For example, for the 2p and 3d ground state orbitals in Kr and $l = 4$, which corresponds to the dip in figure 4, the value of l' in the exchange diagram can be as low as 1. Of course, as l increases, the condition $l' \approx l$ (see equations (34), (35)) removes this anomaly and the asymptotic regime takes over.

Figures 2 and 4 also make it obvious that the $(l + \frac{1}{2})^{-4}$ behaviour sets in relatively late. Therefore, one should be cautious in applying equation (39) to extract the asymptotic constant C from numerical calculations at low l. Thus, when Moncrieff and Wilson (1999) do this at $l = 6$, they obtain a value of $C = 4.799$ which is 1.4 times greater than the true one, $C = 3.440$ (see table 1).

4. Corrections to the single-particle energy and positron annihilation rate

4.1. Single-particle energy

The second-order correction to the single-particle energy $\varepsilon_{n_2 l_2}$ of an electron added to a closed-shell atomic or ionic core can be represented by the diagrams in figure 5 (see, e.g., Amusia and Cherepkov 1975). There are two other second-order diagrams, which contain two holes rather than two particles in the intermediate state. For the present purpose they can be neglected because in these diagrams the angular momentum transferred by the Coulomb interaction is restricted by the angular momenta of the holes, and the diagrams do not contribute to the $l \to \infty$ limit.

Using the same approach as in section 2 it can be shown that the asymptotic expression for the second-order correction to the single-particle energy now takes the form

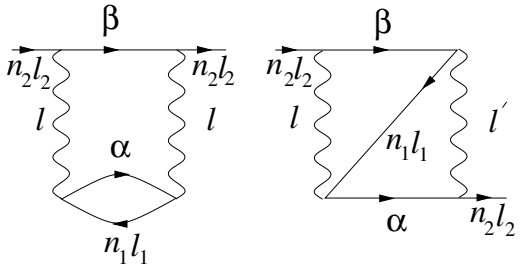

Figure 5. Diagrammatic representation of the second-order correction to the single-particle energy.

$$\Delta\varepsilon^{(l)}_{n_2l_2} = -\frac{3}{16(l+\frac{1}{2})^4}\sum_{n_1l_1}(2l_1+1)\int_0^\infty R^2_{n_1l_1}(r)R^2_{n_2l_2}(r)r^5\,\mathrm{d}r + \mathrm{O}\left(\frac{1}{(l+\frac{1}{2})^6}\right), \tag{47}$$

where the sum includes all core orbitals (cf equations (37)–(39)). The $(l+\frac{1}{2})^{-4}$ convergence pattern is not surprising, since the single-particle energy corresponds to a difference between the total energies of the $N+1$ and N-electron systems.

Note that, as in the total energy, the exchange diagram in the limit of large l equals minus one-half of the direct diagram. If one considers a bound state of a positron with an atomic system (see, e.g., Dzuba *et al* 1995), the upper line in figure 5 will represent the positron and the exchange diagram will be absent. The right-hand side of the asymptotic formula (47) will therefore contain an extra factor of 2.

The diagrams in figure 5 can also represent the second-order correction to the electron or positron scattering amplitude from an atom, if we replace the n_2l_2 state with a continuous spectrum wavefunction[4]. With this modification equation (47) gives the contribution of high transferred angular momenta l to the scattering amplitude. This means that the convergence of scattering calculations obeys the same $(l+\frac{1}{2})^{-4}$ law.

4.2. Positron annihilation

The methods used in this paper can be applied to various quantities. One useful application is a determination of the asymptotic l-dependence of the positron annihilation rate.

The annihilation rate λ, of a positron in a gas of density n is usually expressed in terms of the effective number of electrons (Z_{eff}) of the atom (Fraser 1968) as

$$\lambda = \pi r_0^2 cnZ_{\mathrm{eff}}, \tag{48}$$

where r_0 is the classical radius of the electron and c is the speed of light. Equation (48) defines Z_{eff} as the ratio of the positron annihilation cross section of the atom to the annihilation cross section of a free electron in the Born approximation. Z_{eff} can therefore be written as

$$Z_{\mathrm{eff}} = \sum_{i=1}^{N}\int \left|\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N,\boldsymbol{r}_\mathrm{p})\right|^2\delta(\boldsymbol{r}_i-\boldsymbol{r}_\mathrm{p})\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\ldots\mathrm{d}\boldsymbol{r}_N\,\mathrm{d}\boldsymbol{r}_\mathrm{p}, \tag{49}$$

where $\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N,\boldsymbol{r}_\mathrm{p})$ is the full $(N+1)$-particle wavefunction of the N electron coordinates $\boldsymbol{r}_i$ and positron coordinate $\boldsymbol{r}_\mathrm{p}$. The wavefunction is normalized to a positron plane wave at large positron–atom separations,

$$\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N,\boldsymbol{r}_\mathrm{p}) \simeq \Phi_0(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\mathrm{p}), \tag{50}$$

[4] Multiplied by $-\pi$, these diagrams will give a correction to the scattering phaseshift $\Delta\delta_{l_2}$, for small $\Delta\delta_{l_2}$, if the continuous spectrum wavefunctions are normalized to a δ-function of energy in Ryd (Amusia and Cherepkov 1975).

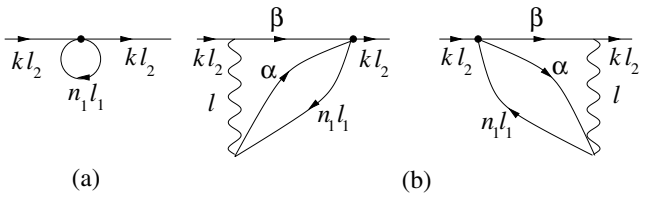

Figure 6. Diagrammatic representation of the zeroth-order $Z_{\rm eff}$ (a) and the first-order corrections to the annihilation vertex (b).

where $\Phi_0(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ is the atomic ground state wavefunction, and $\boldsymbol{k}$ is the incident positron momentum.

In the Hartree–Fock approximation $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N, \boldsymbol{r}_{\rm p})$ is simply the product of the positron wavefunction $\psi_{\boldsymbol{k}}(\boldsymbol{r}_{\rm p})$, which is calculated in the static field of the atom, and the atomic wavefunction $\Phi_0(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$, which is an antisymmetrized product of the single-electron wavefunctions $\psi_{\nu_1}(\boldsymbol{r}_i)$. In the Hartree–Fock approximation equation (49) becomes

$$Z_{\rm eff} = \sum_{\nu_1} \int \left|\psi_{\nu_1}(\boldsymbol{r}_{\rm e})\right|^2 \left|\psi_{\boldsymbol{k}}(\boldsymbol{r}_{\rm p})\right|^2 \delta(\boldsymbol{r}_{\rm e} - \boldsymbol{r}_{\rm p})\, {\rm d}\boldsymbol{r}_1\, {\rm d}\boldsymbol{r}_{\rm p}$$
$$= \sum_{n_1 l_1, l_2} 2(2l_1+1)(2l_2+1) \int R^2_{n_1 l_1}(r) R^2_{k l_2}(r) r^2\, {\rm d}r, \tag{51}$$

where in the last equation the sum runs over all occupied orbitals $n_1 l_1$, as well as the positron partial waves l_2, and the positron radial wavefunction is normalized by $R_{kl_2}(r) \simeq \sin(kr - \frac{\pi}{2} l_2 + \delta_{l_2})/kr$. Equation (51) is represented diagrammatically in figure 6(a). It is easy to check that besides the usual diagrammatic rules, in calculating the contribution of a given positron partial wave l_2 to $Z_{\rm eff}$ we must use $[4\pi(2l_2+1)]^{1/2} R_{kl_2}(r) Y_{l_2 m_2}(\hat{\boldsymbol{r}}) \equiv \psi_{k l_2}(\boldsymbol{r})$ and its complex conjugate for the initial and final positron lines, respectively.

This approximation is not sufficient to accurately describe positron annihilation. A better positron wavefunction must be used, which accounts for the positron–atom correlation potential. However, it is also necessary to include corrections to the positron annihilation vertex (Dzuba *et al* 1993, 1996). Figure 6(b) shows the two first-order corrections to the vertex. They are of equal value, and their sum can be be written as

$$\Delta Z_{\rm eff} = 2 \sum_{\alpha, \beta, n_1 l_1} \frac{2\langle n_1 l_1, k l_2 | \delta(\boldsymbol{r}_{\rm e} - \boldsymbol{r}) | \alpha, \beta \rangle \langle \alpha, \beta | V | n_1 l_1, k l_2 \rangle}{\varepsilon - \varepsilon_\alpha - \varepsilon_\beta + \varepsilon_{n_1 l_1}}, \tag{52}$$

where $\varepsilon = k^2/2$ is the positron energy, α and β are excited electron and positron states, respectively, the sum over the ground state electron orbitals $n_1 l_1$ also implies summation over $m_1 = -l_1, \ldots, m_1$, and an extra factor 2 accounts for the electron spins.

The asymptotic behaviour of the contribution of high-angular-momentum states α and β, i.e. large l, is considered in the same way as earlier in the paper. We first expand the delta function as

$$\delta(\boldsymbol{r}_{\rm e} - \boldsymbol{r}_{\rm p}) = \sum_{l=0}^{\infty} \delta^{(l)}_{\rm ep} = \sum_{l=0}^{\infty} \frac{1}{r_{\rm e}^2} \delta(r_{\rm e} - r_{\rm p}) \frac{2l+1}{4\pi} P_l(\cos\theta). \tag{53}$$

In a similar manner to equation (29), the contribution of the transferred angular momentum l to $\Delta Z_{\rm eff}$ is

$$\Delta Z^{(l)}_{\rm eff} = 4 \sum_{n_1 l_1 m_1} \langle \psi_0 | \delta^{(l)}_{\rm ep}(-r^{(l)}_{\rm ep}/2) | \psi_0 \rangle, \tag{54}$$

where $\psi_0 = [4\pi(2l_2+1)]^{1/2} R_{kl_2}(r_\mathrm{p}) Y_{l_2 m_2}(\hat{\boldsymbol{r}}_\mathrm{p}) R_{n_1 l_1}(r_\mathrm{e}) Y_{l_1 m_1}(\hat{\boldsymbol{r}}_\mathrm{e})$, and the minus sign is a consequence of the electron–positron Coulomb interaction being attractive. As in section 2, we can replace r_e by $r(1+\sigma)$ and r_p by $r(1-\sigma)$, and use

$$\delta^{(l)}_\mathrm{ep} = \frac{1}{2r^3}\delta(\sigma)\frac{2l+1}{4\pi}P_l(\cos\theta) \tag{55}$$

together with equations (16) and (17), to calculate the matrix element in equation (54). This gives the asymptotic form of the first-order correction to Z_eff in a given positron partial wave l_2,

$$\Delta Z^{(l)}_\mathrm{eff} \simeq \frac{2l_2+1}{(l+\frac{1}{2})^2}\sum_{n_1 l_1} 2(2l_1+1)\int_0^\infty R^2_{n_1 l_1}(r) R^2_{kl_2}(r) r^3\,\mathrm{d}r. \tag{56}$$

Therefore, in calculations based on partial-wave expansions about a single centre the annihilation rate Z_eff converges much more slowly than the energy. Equation (56) shows also that inclusion of ever higher angular momenta increases the value of Z_eff, since $\Delta Z^{(l)}_\mathrm{eff}$ are positive. The coefficient in the asymptotic form of $\Delta Z^{(l)}_\mathrm{eff}$ depends on the overlap of the electron and positron densities. A similar integral determines the coefficient in the $(l+\frac{1}{2})^{-2}$ drop of the contribution of the relativistic Breit interaction to the correlation energy of He-like ions (Ottschofski and Kutzelnigg (1997), equation (5.7)).

The positron annihilation rate in a bound state, Γ is given by an integral identical to that in equation (49) times $\pi r_0^2 c$. In this case Ψ is the total wavefunction of the positron–atom bound state. As follows from the above analysis, convergence of the annihilation vertex corrections to Γ is of the form

$$\Delta\Gamma^{(l)} \simeq \frac{C_\Gamma}{(l+\frac{1}{2})^2}, \tag{57}$$

where

$$C_\Gamma = \frac{\pi r_0^2 c}{4\pi}\sum_{n_1 l_1} 2(2l_1+1)\int_0^\infty R^2_{n_1 l_1}(r) R^2_p(r) r^3\,\mathrm{d}r, \tag{58}$$

and $R_\mathrm{p}(r)$ is the radial wavefunction of the bound positron.

Mathematically, the difference between the $(l+\frac{1}{2})^{-4}$ asymptotic behaviour of the correlation corrections to the energy and $(l+\frac{1}{2})^{-2}$ drop of the annihilation rate is a result of replacing the second Coulomb interaction in the diagrams of figure 5 with a δ-function. Comparison of equations (3) and (53) shows that the latter has an extra $2l+1$ factor, while the presence of $\delta(\sigma)$ eliminates $l+\frac{1}{2}$ in the denominator, cf equation (24).

Just as for the energy corrections, the asymptotic $(l+\frac{1}{2})^{-2}$ decrease of the high-l contributions to the annihilation rate established by means of perturbation theory must hold in nonperturbative calculations. Qualitatively, very slow convergence of the annihilation rates with respect to the maximal orbital angular momentum l_max in CI calculations of systems containing positrons has been known for a while (Strasburger and Chojnacki 1995, Mitroy and Ryzhikh 1999, Bromley *et al* 2000). However, the true value of p in the $1/l^p_\mathrm{max}$ dependence of the rate increments has never been established (see section 5).

A common feature of all asymptotic expressions is that the two particles which exchange a high angular momentum l through the Coulomb interaction are 'pulled together' by the cusplike singularity in $V^{(l)}$, or the δ-function of the annihilation vertex. As a result, the coefficients in the asymptotic formulae depend on the wavefunctions taken at the same point. This makes it is easy to guess the form of the nonperturbative answer from a perturbation-theory expression, cf equations (25) and (41). Thus, in a system containing one electron and one positron in an

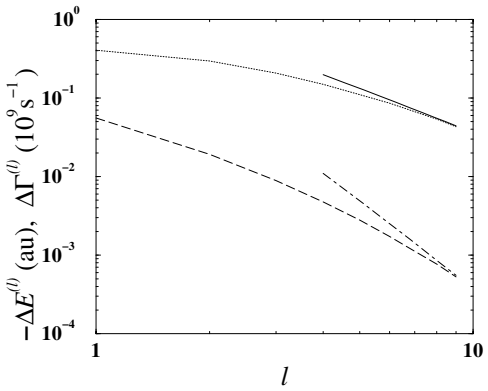

Figure 7. Increments of the total energy and annihilation rate for PsH from Mitroy *et al* (2001), plotted against l, with asymptotic curves fitted at high l: — — —, $\Delta E^{(l)}$; — · —, $4.5/(l+\frac{1}{2})^4$; · · · · · ·, $\Delta\Gamma^{(l)}$; ——, $4/(l+\frac{1}{2})^2$.

S state the asymptotic increments of the spin-averaged annihilation rate will be given by (57) with

$$C_\Gamma = 4\pi^2 r_0^2 c \int_0^\infty |\Psi(\boldsymbol{r},\boldsymbol{r})|^2 r^3 \,\mathrm{d}r, \tag{59}$$

where $\Psi(\boldsymbol{r}_\mathrm{e},\boldsymbol{r}_\mathrm{p})$ is the wavefunction of the system. Practically, such an equation could be applied to systems like e^+Li or e^+Na, where the electron–positron pair moves in the field of a relatively inactive core (see the appendix).

5. Analysis of convergence of the energy and annihilation rate of PsH

To illustrate the slower convergence of the annihilation rate we examine the results of CI calculations performed for the PsH system (Bromley *et al* 2000, Mitroy *et al* 2001). These give both the annihilation rate Γ and the total energy E for calculations with successively larger l values[5]. It should be noted again that a perturbative derivation of $\Delta E^{(l)}$ and $\Delta\Gamma^{(l)}$ is still valid for a CI calculation, as the orbitals with higher l values only make a small contribution. Thus, although the coefficients in a nonperturbative treatment may differ from those in equations (39) and (57), the asymptotic l dependence of the corresponding increments should remain the same.

Figure 7 shows that numerical $\Delta E^{(l)}$ and $\Delta\Gamma^{(l)}$ do indeed converge towards their respective asymptotic forms $C(l+\frac{1}{2})^{-4}$ and $C_\Gamma(l+\frac{1}{2})^{-2}$. However, this convergence is very slow. It only becomes apparent near the largest value of $l = 9$, see figure 7. Note that we can use equations (41) and (59) to make rough estimates of the constants C and C_Γ (see appendix).

A more detailed examination of the l-dependence of $\Delta E^{(l)}(l+\frac{1}{2})^4$ in fact shows that even at $l = 9$ this quantity is not constant. On the other hand, the behaviour of $\Delta\Gamma^{(l)}(l+\frac{1}{2})^2$ may indicate a loss of numerical accuracy at such high l values. The latter is supported by the fact that even after extrapolation to $l = \infty$ the value of Γ is still 10% below the correct one (Mitroy *et al* 2001).

The slow evolution of $\Delta E^{(l)}$ and $\Delta\Gamma^{(l)}$ towards their asymptotic forms can probably be explained as follows. According to perturbation theory, the coefficients in equations (39) and (57) are determined by the zeroth-order wavefunctions. In a nonperturbative calculation for

[5] More precisely, they present E and Γ as functions of l_max. However, this difference does not affect the leading-order l dependence of the increments $\Delta E^{(l)}$ and $\Delta\Gamma^{(l)}$.

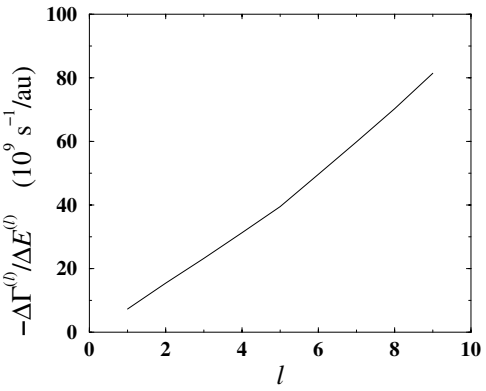

Figure 8. Ratio of $\Delta\Gamma^{(l)}$ to $\Delta E^{(l)}$ as a function of the maximal angular momentum l included in the CI calculation by Mitroy *et al* (2001).

a given $l_{\max} = l$ the coefficient in the asymptotic formula is determined by the wavefunction at zero interparticle distance ($\boldsymbol{r}_1 = \boldsymbol{r}_2$, or $\boldsymbol{r}_\mathrm{e} = \boldsymbol{r}_\mathrm{p}$), obtained at this stage. Therefore, it keeps changing as more partial waves are included in the calculation. This effect is especially important for systems containing positrons, because the wavefunction is enhanced at $\boldsymbol{r}_\mathrm{e} = \boldsymbol{r}_\mathrm{p}$ due to the Coulomb attraction between the particles. This enhancement also explains the large size of the high-l contributions in such systems. On the other hand, if one looks at the ratio, $\Delta\Gamma^{(l)}/\Delta E^{(l)}$, the drift of the wavefunction should be largely eliminated. This ratio is plotted in figure 8 as a function of l.

Figure 8 is a clear illustration of the slower convergence of the annihilation rate, as compared with the energy. It also confirms that the ratio is superlinear with respect to $l + \frac{1}{2}$, although the asymptotic $(l + \frac{1}{2})^2$ behaviour is not obvious. This may partly be because of the numerical convergence problems mentioned above.

6. Concluding remarks

In this paper we have studied the problem of convergence of the correlation corrections to the total and single-particle energies and positron annihilation rates, with respect to the single-particle angular momenta.

We have derived an asymptotic formula for the second-order perturbation energy for closed-shell atoms at high transferred angular momenta l. A $1/(l + \frac{1}{2})^4$ dependence has been found. The formula reduces to Schwartz's formula for two-electron atoms when hydrogenic $1s^2$ wavefunctions are used. By testing the formula for Ne and Kr we have demonstrated that it agrees very well with the numerical results. These results also show that B-splines are an excellent means of spanning the energy continuum. In other words, they provide a finite single-particle basis which is effectively complete. On the other hand, we have identified the limitations of such bases for very high l. They are related to the cusplike singularity of the Coulomb interaction for high transferred angular momenta, and to the choice of a certain B-spline knot sequence.

The general method employed in the first part of the paper has been applied to the problem of positron annihilation on atoms. We have shown that the correlation corrections to the annihilation rate have a much slower $1/(l + \frac{1}{2})^2$ dependence. The results of CI calculations of the energy and annihilation rates of PsH by Mitroy *et al* (2001) converge towards the predicted asymptotic behaviour.

Qualitatively, our analysis explains the origin of the notoriously slow convergence of the energies and especially annihilation rates for systems containing positrons. With little effort the method we apply can be used to derive nonperturbative ('exact') asymptotic formulae. In general, they show the same l-dependence, with the coefficient given by an expectation value of the contact two-particle density.

The knowledge of the asymptotic behaviour can be used to test the accuracy and convergence of numerical calculations. It can also be applied to extrapolate correctly the contributions of high angular momenta, and account for all angular momenta beyond those explicitly included in the numerical calculation. Such a procedure is especially important in cases where convergence is slow.

Acknowledgments

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Appendix. Asymptotic forms of the energy and annihilation rate for bound Ps

Let us consider a positron bound state with an atom (negative ion) whose ionization potential (electron affinity) is smaller than the binding energy of the ground state positronium atom (Ps), $|E_{1s}| = 6.8$ eV. In this case the lowest dissociation threshold of the system is that into the positive ion (neutral atom) and Ps(1s). If the binding energy is small, the weakly bound Ps moves mostly far away from the core and can be described by a normalized wavefunction

$$\Psi(\boldsymbol{r}_e, \boldsymbol{r}_p) = \sqrt{\frac{\kappa}{2\pi}}\frac{e^{-\kappa R}}{R}\varphi_{1s}(\boldsymbol{r} - \boldsymbol{r}_p) \tag{A.1}$$

where $\boldsymbol{R} = (\boldsymbol{r}_e + \boldsymbol{r}_p)/2$ is the centre-of-mass coordinate of the positronium atom relative to the nucleus, φ_{1s} is the internal Ps wavefunction and κ is related to the binding energy by $E_b = \kappa^2/2M$, where $M = 2$ au is the Ps mass.

Using this wavefunction in equations (41) and (59) we obtain

$$C = \frac{9\pi|\varphi_{1s}(0)|^2}{8\kappa^3}, \tag{A.2}$$

$$C_\Gamma = \frac{\pi r_0^2 c|\varphi_{1s}(0)|^2}{2\kappa}, \tag{A.3}$$

where $|\varphi_{1s}(0)|^2 = 1/8\pi$, and the factor $\pi r_0^2 c|\varphi_{1s}(0)|^2$ is simply the spin-averaged annihilation rate of the ground state positronium and has a known value of 2.0×10^{-9} s^{-1} (Berestetskii *et al* 1982). Equations (A.2) and (A.3) show that for more weakly bound systems (smaller κ) the contribution of high partial waves l is greater.

Let us apply equations (A.2) and (A.3) to PsH which has a binding energy of $E_b = 0.0392$ au (Ryzhikh *et al* 1998). This leads to $\kappa = 0.396$, and gives asymptotic constants $C = 2.3$ au and $C_\Gamma = 2.5 \times 10^{-9}$ s^{-1}, which are good estimates of the values inferred from the CI calculations of Mitroy *et al* (2001) (see the caption of figure 7).

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