Asymptotic behavior of atomic and molecular wave functions

(extended Koopmans' theorem/density matrix)

J. KATRIEL[†] AND E. R. DAVIDSON

Department of Chemistry, University of Washington, Seattle, Washington 98195

ABSTRACT   The asymptotic form of bound-state wave functions is derived by analytic continuation of asymptotic scattering-state wave functions. The result is also rigorously derived by using an approach that is independent of scattering theory. One aspect of the result is that the N electron wave function becomes the lowest accessible exact wave function for the remaining $N - 1$ electrons when one electron is far away from all the nuclei. This shows that the recently developed extended Koopmans' procedures are in principle exact for the first ionization energy.

The long-range asymptotic behavior of bound-state wave functions has been the focus of a significant research effort (1–8). The pioneering discussion of the asymptotic behavior of Hartree–Fock orbitals by Handy et al. (1) contains several important ingredients of a more general analysis. The long-range behavior of natural orbitals was investigated by Morrell et al. (2) and by Davidson (3). Upper bounds to the long-range behavior of ground state densities were derived and improved by several investigators (4). The upper bound derived by Hoffmann-Ostenhof and Hoffmann-Ostenhof (4) actually has the same exponential dependence as the exact result derived here, and they also conjectured, but did not prove, the correct form of the preexponential factor. More recently, Silverstone et al. (6, 7) examined the asymptotic behavior of the helium ground state natural orbitals, obtaining some further analytical results (6) and essentially confirming them numerically (7).

The detailed asymptotic behavior of scattering states, which is crucial in the very formulation of the corresponding theory, is considerably easier to obtain than that for bound states. The scattering matrix has poles corresponding to the bound-state eigenvalues, at which the eigenfunctions become bound-state eigenfunctions. This can be used to extract the asymptotic form of the bound-state wave functions starting from the scattering wave functions and evaluating them at the poles of the scattering matrix. This is done below. An independent derivation, which does not rely on scattering theory results, is presented following that, and some consequences of the form of the results are discussed.

Asymptotic form of bound state wave functions

We shall consider a system with $N - 1$ bound electrons and total nuclear charge Z, which is initially in its ground state with energy E_0^{N-1}. An incoming electron with energy $\hbar^2 k_0^2/2m$ can be scattered into either the elastic channel or any one of the inelastic channels, provided that its energy is high enough. The asymptotic form in a channel involving excitation of the $N - 1$ electron system to its nth excited state will be, in a.u.,

$$\psi_n^{N-1} [\delta_{n,o}\phi_{in} - S_{on}r^{-1}e^{i(k_nr + \eta_n\log r)}] \xi \quad n = 0, 1, \ldots \quad [1]$$

where

$$k_n^2/2 + E_n^{N-1} = k_0^2/2 + E_0^{N-1} \equiv E$$

$$\eta_n = Z^*/k_n, \quad Z^* = Z - (N - 1),$$

ϕ_{in} is the incoming wave, S_{on} is the S-matrix element, and ξ is the spin and angular function of the scattered electron.

Now, all the elements of the scattering matrix have a pole when E, the total energy of the system, becomes equal to a bound-state energy of the N electron system—say, $E = E_m^N$. At such an energy we obtain

$$k_n = \sqrt{2(E_m^N - E_n^{N-1})} \equiv iK_{mn}$$

where K_{mn} is real and positive.

The long-range behavior is determined by the exponential depending on K_{mo}, which corresponds to ionization into the ground state of the $N - 1$ electron system, as this is the most slowly decaying one. Comparison with Eq. 1 suggests that the asymptotic result is

$$\psi_m^N(r_1, r_2, \ldots, r_N) \, r_1 \overset{\cong}{\to} \infty \, \psi_0^{N-1}(r_2, \ldots, r_N) \, r_1^\beta e^{-\alpha r_1} \xi \quad [2]$$

where

$$\alpha = K_{mo} \quad \text{and} \quad \beta = [Z - (N - 1)]/\alpha - 1. \quad [3]$$

For the ground state of the N electron system $\alpha = \sqrt{2\epsilon}$, where ϵ is the first ionization potential. For an excited state α involves the ionization energy from this excited state into the ground state of the $N - 1$ electron system. Hence, the excited state is asymptotically more diffuse than the ground state, a result which is not at all unexpected.

We note in passing that if the ground state of the $N - 1$ electron system is inaccessible from ψ_m^N, say, because their spins differ by more than $1/2$, our discussion has to be modified so as to consider, in Eq. 1, an initial $N - 1$ electron system which is accessible from ψ_m^N. Only for such an $N - 1$ electron system will $E = E_m^N$ correspond to a pole in the S matrix. The exponential coefficient will involve the ionization energy into the lowest accessible state of the $N - 1$ electron system, which may be different for different states of the N electron system. This point was discussed in detail by Hoffmann-Ostenhof and Hoffmann-Ostenhof (4) and is more completely treated in the following section.

A purely bound-state derivation

A derivation of the asymptotic form of bound-state wave functions which does not depend on the scattering state asymptotic wave functions and on the conjecture concerning the poles of the analytically continued S matrix, will now be presented.

† Permanent address: Department of Chemistry, Technion–Israel Institute of Technology, Haifa 32000, Israel.

Let $\psi_i^{N-1}(2\ldots N)$ be an exact eigenfunction of $H^{N-1}(2\ldots N)$. Since the ψ_i^{N-1} form a complete set, one can expand an exact bound-state eigenfunction $\psi^N(1\ldots N)$ of $H^N(1\ldots N)$ as

$$\psi^N = \sum f_i(1)\psi_i^{N-1}(2\therefore N) \qquad [4]$$

where the summation includes integration over the $N-1$ particle continuum. In this expansion the f_i are the Fourier coefficients

$$f_i = \langle \psi_i^{N-1}|\psi^N\rangle_{N-1} \qquad [5]$$

of the orthonormal ψ_i^{N-1}. The f_i are nonorthogonal, non-normal, and generally linearly dependent. The expression $\langle\ \rangle_{N-1}$ denotes integration over the spin and space coordinates of electrons $2\ldots N$.

Now suppose H is approximated by

$$H^N = \sum_{i=1}^{N} h(i) + \sum_{i<j} r_{ij}^{-1} \qquad [6]$$

where

$$h(i) = -\frac{1}{2}\nabla_i^2 + V_{en}(i) \qquad [7]$$

and V_{en} is the electron-nuclear Coulomb interaction. Then

$$H^N(1\ldots N) = H^{N-1}(2\ldots N) + h(1) + \sum_{i>1} r_{i1}^{-1}. \qquad [8]$$

By definition

$$H^N\psi^N = E^N\psi^N \qquad [9]$$

where E^N is any one of the exact bound-state eigenvalues. Then

$$\langle \psi_i^{N-1}|H^N\psi^N\rangle = E^N\langle \psi_i^{N-1}|\psi^N\rangle. \qquad [10]$$

Inserting expression 8 for H^N and using the Hermitian property and eigenvalue property

$$H^{N-1}\psi_i^{N-1} = E_i^{N-1}\psi_i^{N-1} \qquad [11]$$

of H^{N-1} gives

$$h(1)f_i(1) + \langle \psi_i^{N-1}\,|\sum_{j>1} r_{j1}^{-1}|\psi^N\rangle_{N-1} = -I_i f_i \qquad [12]$$

where

$$I_i = E_i^{N-1} - E^N. \qquad [13]$$

For convenience we will assume that the I_i are ordered so that $I_i \le I_{i+1}$. The I_i are the ionization energies from the state E^N of the N electron system into the various states of the ion.

Let us define

$$W_i = [r_1^{-1}f_i - \langle \psi_i^{N-1}|r_{12}^{-1}|\psi^N\rangle_{N-1}] \qquad [14]$$

and note that $\langle \psi_i^{N-1}|r_{j1}^{-1}|\psi^N\rangle$ is the same for all j, so that Eq. 12 can be written as

$$[h + (N-1)r^{-1} + I_i]f_i = (N-1)W_i. \qquad [15]$$

From the Laplace expansion for r_{12}^{-1}

$$r_{12}^{-1} = \sum_L \frac{r_<^L}{r_>^{L+1}} P_L(\cos\theta_{12}). \qquad [16]$$

We get for large r_1

$$\langle \psi_i^{N-1}|r_{12}^{-1}|\psi^N\rangle \simeq \sum_L r_1^{-L-1}\langle \psi_i^{N-1}|r_2^L P_L(\cos\theta_{12})|\psi^N\rangle_{N-1}. \qquad [17]$$

Inserting the expansion of ψ^N (Eq. 4) gives

$$\langle \psi_i^{N-1}|r_{12}^{-1}|\psi^N\rangle \simeq \sum_L \sum_j r_1^{-L-1}f_j(1)$$
$$\times \langle \psi_i^{N-1}|r_2^L P_L(\cos\theta_{12})|\psi_j^{N-1}\rangle. \qquad [18]$$

By the orthogonality of the ψ_i^{N-1}, the $L=0$ term reduces to $r_1^{-1}f_i(1)$, so

$$W_i \simeq -\sum_j f_j(1)\sum_{L>0} r_1^{-L-1}$$
$$\times \langle \psi_i^{N-1}|r_2^L P_L(\cos\theta_{12})|\psi_j^{N-1}\rangle. \qquad [19]$$

Now consider the asymptotic solution to the homogeneous equation

$$[h + (N-1)r^{-1} + I_i]f_i = 0 \qquad [20]$$

where r is measured from the center of nuclear charge and $r \gg R$ where R is the maximum distance between nuclei. Then V_{en} approaches $-Qr^{-1}$ where Q is the total nuclear charge. The asymptotic solution to this equation is well known to be

$$f_i \simeq r^{\beta_i}e^{-\alpha_i r}\xi \qquad [21]$$

where

$$\alpha_i = \sqrt{2I_i} \quad \text{and} \quad \beta_i = (Q-N+1)/\alpha_i - 1. \qquad [22]$$

For the coupled Eqs. 15 it is now clear that, except possibly for $i=1$, the coupling term W_i may contain terms which die exponentially only like $\exp(-\alpha_1 r)$; and hence for large r, W_i may determine the asymptotic form. Suppose the functions f_i are partitioned into sets by examining their connectivity graph. To this end, two indices i and j will be regarded as connected if

$$W_i = -\sum_j f_j(1)W_{ij} \qquad [24]$$

has a nonzero W_{ij}. Indices forming part of the same connected graph will then form a set which can be labeled by $I = \inf\{i\}$. Following the similar arguments of Handy et al. (1) and Silvertone et al. (6), all f_i in the same set I will have an exponential dependence $\exp(-\alpha_I r)$ with

$$\alpha_I = \min_{i\epsilon I} \alpha_i. \qquad [25]$$

While these arguments are typical of the derivation of asymptotic forms in mathematical physics, there are some logical difficulties. Ahlrichs (8) has emphasized the well-known fact that any function can be expanded in terms of any complete set of functions, so the leading term in an expansion need not reflect the limiting form. As discussed below, infinite sum **24** can be viewed as a Laurant series (multiplied by an exponential) which contains only one term in the highest power of r. Hence, we will assume that this term governs the asymptotic form.

For example, in the absence of spin-orbit coupling, the state ψ^N will correspond to some value of S and summation **4** will include only ψ_i^{N-1} corresponding to $S \pm \frac{1}{2}$. The coupling between $f_i^{S+1/2}$ and $f_j^{S-1/2}$ is zero, however, so the $f^{S-1/2}$ and $f^{S+1/2}$ will have different exponential behaviors.

If f_i and f_j are connected, then there is some smallest value of L in

$$W_{ij} \simeq \sum_{L>0} r_1^{-L-1}\langle \psi_i^{N-1}|r_2^L P_L(\cos\theta_{12})|\psi_j^{N-1}\rangle \qquad [26]$$

which makes a nonvanishing contribution. Let us denote this least L by L_{ij}. Then, for any pair of fs in the set I—say, f_p and f_q—there will be various paths in the connectivity graph from

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p to q. Along each of these paths $p \to a \to b \to \ldots \to q$ one can sum the L_{ij}. Then let us define

$$L_p^* = \text{min over all paths connecting } p \text{ to } I \ \{\textstyle\sum (L_{ij} + 1)\}. \quad [27]$$

From the equation for f_I it is clear that the coupling terms vanish faster than f_I/r^2 so that the value of β is determined by the homogeneous equation and hence is β_I. For the other members f_i of the set I the value of β_i is determined by the coupling terms, so it is the largest of the $\beta_j - L_{ij} - 1$. Continuing this argument gives

$$\beta_i = \beta_I - L_i^*. \quad [28]$$

For molecules of no symmetry L_i^* will be 2, but for some of the f_i of some high-symmetry atoms or molecules, L_i^* will be >2.

Let us now consider only the f_i that are nonvanishing; that is, we consider only the ψ_i^{N-1} for which $f_i\psi_i^{N-1}$ can have a component of the same symmetry as ψ^N. Let us assume that only such ψ_i^{N-1} are included in 4 and that ψ_1^{N-1} denotes the lowest accessible state of the $N - 1$ electron system. Then

$$f_i/f_1 \simeq r^{-L^*} \quad \text{with} \quad L^* \ge 2$$

if i is in set 1 and

$$f_i/f_1 \simeq e^{-(\alpha_I - \alpha_1)r} \quad \text{and} \quad \alpha_I > \alpha_1$$

if i is not in set 1. It follows that

$$\psi^N \simeq f_1(1) \, \psi_1^{N-1}(2 \ldots N)$$

$$\text{where} \quad f_1 \simeq r_1^{\beta_1} e^{-\alpha_1 r_1}[1 + \mathcal{O}(r_1^{-1})]. \quad [29]$$

This result is identical with Eq. 2. An immediate consequence is that $\rho(r_1, r_1') \simeq f_1(1)f_1^*(1')$ for either r_1 or r_1' large,

$$\text{and} \quad \rho(r_1) \simeq |f_1(1)|^2[1 + \mathcal{O}(r^{-4})].$$

For atoms with ψ_i^{N-1} having angular momentum L_i,

$$L_{ij} = \begin{cases} |L_i - L_j| & \text{if } L_i \ne L_j \\ 2 & \text{if } L_i = L_j > 0 \end{cases}.$$

States with $L_i = L_j = 0$ are unconnected. If f_I has $L_I = 0$, then other $L_i = 0$ states in this set will have $L_i^* \ge 4$ since they can only connect via a two-step path involving a nonzero intermediate L_a.

For two electron systems, all of the f_i of the same spin are in the same connected set so

$$\begin{aligned} f_{1s} &\simeq r^\beta e^{-\alpha r} \\ f_{js} &\simeq r^{\beta-4} e^{-\alpha r} \quad j > 1 \\ f_{jl} &\simeq r^{\beta-l-1} e^{-\alpha r} \quad l \ge 1 \end{aligned} \quad [30]$$

Relations 30 have been numerically verified by evaluating the f_is using the natural orbital expansion of Davidson (9). Further analysis in this case shows that the leading correction to f_{1s} is $-\beta(\beta + 1)/(2\alpha)r^{\beta-1}e^{-\alpha r}$. By expressing the natural orbitals in terms of the f_i, it becomes evident that f_{1s} is mixed into all the s-type natural orbitals, so that they all have the same long-range behavior.

Discussion of the asymptotic form

One remarkable consequence of the comparison between the present result and that of Morrell et al. (2) is that their μ_{max} is indeed rigorously identical with the exact ionization potential, which means that the wave function they generated for the $N - 1$ electron ground state by annihilating orbitals in the ground state of the N electron system is the exact solution for the former.

This very surprising and pleasing result does not imply that

the set of $N - 1$ electron functions, ϕ_i^{N-1}, complementary to the natural orbitals, χ_i, of the ground state of the N electron system form a complete set for $N - 1$ electrons. On the contrary, by a dimensionality argument, it is clear that these functions are incomplete in the $N - 1$ electron space (10). All that this result does imply is that the ground state of the $N - 1$ electron system is contained in the space spanned by those complementary functions. Moreover, the expansion coefficients, $\langle \psi_0^{N-1} | \phi_i^{N-1} \rangle$, of the $N - 1$ electron ground state in terms of these functions are determined by substituting in Eq. 2 the Carlson–Keller (11) expansion for the N-electron ground state,

$$\psi_0^N(r_1, r_2, \ldots, r_N) = \sum_i n_i^{1/2} \, \chi_i(r_1) \, \phi_i^{N-1}(r_2, r_3, \ldots, r_N). \quad [31]$$

Hence, the coefficients are asymptotically proportional to $n_i^{1/2}\chi_i$. An immediate consequence is that the formalism of ref. 2, and the closely related extension of Koopmans' theorem suggested by Smith and Day (12), will generate the exact ionization potential, provided that the exact N-electron ground state wave function is used. This point was very clearly discussed by Levy and Parr (13) and by Silverstone et al. (6). The latter authors' results for the asymptotic behavior of the helium ground state natural orbitals—in particular, the fact that the $l > 0$ natural orbitals decay more rapidly than the s-type natural orbitals—show that, as r_2 becomes large, $\psi(1, 2)$ considered as a function of r_1 becomes an s-type wave function consisting of a superposition of all the s-type natural orbitals. The coefficients in this expansion are given, relative to the first one, as

$$C_i/C_1 = [n_i/n_1]^{1/2} \lim_{r \to \infty} [\chi_i(r)/\chi_0(r)] \quad [32]$$

where n_i is the occupation number of the ith natural orbital, $\chi_i(r)$.

Silverstone et al. (6) pointed out that the exponential coefficient in their asymptotic expression for the natural orbitals can only be equal to $\sqrt{2\epsilon}$, where ϵ is the exact ionization potential, if the above expansion is asymptotically equal to the ground state of He^+, e^{-2r}—i.e.,

$$C_i/C_1 = \langle 1sHe^+ | \chi_i \rangle / \langle 1sHe^+ | \chi_1 \rangle. \quad [33]$$

Our result shows that this is indeed the case. To illustrate this point we have evaluated C_i/C_1 from both Eq. 32 and Eq. 33, using Davidson's (9) natural orbitals. From Eq. 33 we obtained, for $i = 2,3,4,5$, the ratios 0.178, 0.037, −0.013, and −0.006, which compare reasonably well with the values obtained using Eq. 32: 0.179, 0.035, −0.012, and −0.005. We extracted the latter sequence of numbers by evaluating the natural orbitals at values of $r(\simeq 6 \text{ a.u.})$ for which they are already "asymptotic" but still reliable. They agree with the estimates for these ratios presented by Carroll et al. (7). As a further examination of the conclusion that the ground state wave function of helium behaves like

$$\psi(1,2) \simeq e^{-2r_2}r_1^\beta e^{-\sqrt{2\epsilon_I}r_1} \quad [34]$$

when electron one is far away, where

$$\beta = 1/\sqrt{2\epsilon_I} - 1,$$

we computed the ratio between the left-hand expression and the right-hand side expression in Eq. 34, for $r_2 < r_1$. This ratio is fairly close to constant for $r_1 \sim 5$ a.u. and $0 < r_2 < 1$ a.u. (to about 0.05% for $\theta_{12} = \pi/2$, some angular dependence being observed for the above r_1 and $r_2 > 0.5$). For $\psi(1,2)$ we used Davidson's (9) improved Kinoshita-type 44-term wave function. Even this wave function is not very accurate for r_1 or r_2 larger than about 5 a.u.

Note Added in Proof. Lassettre (14) gave a less detailed proof of Eq. 2.

1. Handy, N. C., Marron, M. T. & Silverstone, H. J. (1969) *Phys. Rev.* **180,** 45–48.
2. Morrell, M. M., Parr, R. G. & Levy, M. (1975) *J. Chem. Phys.* **62,** 549–554.
3. Davidson, E. R. (1976) *Reduced Density Matrices in Quantum Chemistry* (Academic, New York).
4. Hoffmann-Ostenhof, M. & Hoffmann-Ostenhof, T. (1977) *Phys. Rev. A* **16,** 1782–1785.
5. Tal, Y. (1978) *Phys. Rev. A* **18,** 1781–1783.
6. Silverstone, H. J., Carroll, D. P. & Metzger, R. M. (1979) *J. Chem. Phys.* **70,** 5919–5921.
7. Carroll, D. P., Silverstone, H. J. & Metzger, R. M. (1979) *J. Chem. Phys.* **71,** 4142–4163.
8. Ahlrichs, R. (1976) *J. Chem. Phys.* **64,** 2706–2707.
9. Davidson, E. R. (1963) *J. Chem. Phys.* **39,** 875–880.
10. Smith, V. H. & Ohrn, Y. (1974) in *Reduced Density Operators with Applications to Physical and Chemical Systems-II,* ed. Erdahl, R. M., Queen's Papers in Pure and Applied Mathematics No. 40 (Queen's University, Kingston, ON), p. 193.
11. Carlson, B. C. & Keller, J. M. (1961) *Phys. Rev.* **121,** 659–661.
12. Smith, D. W. & Day, O. W. (1975) *J. Chem. Phys.* **62,** 113–114.
13. Levy, M. & Parr, R. G. (1976) *J. Chem. Phys.* **64,** 2707–2708.
14. Lassettre, E. N. (1965) *J. Chem Phys.* **43,** 4479–4486.