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New variation-perturbation principle for two-particle interactions

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A revised formulation of the variation-perturbation method is given for two-particle interactions. Calculations with this technique require an amount of labor comparable to the traditional one, but appear to converge more rapidly. For ground states, the procedure generates a lower bound to the second-order energy, complementing the upper bound supplied by the usual method.

In the perturbation-theoretic approach to the problem of calculating bound states, the exact Hamiltonian is partitioned into H_0+H', where the corresponding problem for H_0 is assumed to be exactly solvable, and corrections are made for the presence of the perturbation H'. For corrections higher than first order in the strength of H', summations over off-diagonal matrix elements of H' are prescribed. In particular, the second-order correction to the energy is given by

$$E_2=\sum_k \frac{|H'_{ik}|^2}{E_i-E_k}\ ,\tag{1}$$

where E_i and E_k are the unperturbed energies of $|i\rangle$ and $|k\rangle$, H'_{ik} is the matrix element of H' connecting them, and the summation spans all bound and continuum states. A number of procedures are, at least in principle, available to evaluate E_2. One may simply compute the indicated matrix elements and explicitly carry out the addition. This is the simplest method, and is most effective when the summation converges rapidly. A much more elegant procedure is to solve an inhomogeneous Schrödinger equation[1-3] to calculate ψ_1, the correction to the wave function of $|i\rangle$ linear in the strength of H':

$$(H_0-E_i)\psi_1=-(H'-E_1)\psi_0\ ,\tag{2a}$$

or

$$\psi_1=GH'\psi_0\tag{2b}$$

and

$$E_2=(\psi_1^*H'\psi_0)\ ,\tag{2c}$$

where E_1, E_2 are the first- and second-order corrections to the energy of $|i\rangle$, ψ_0 the unperturbed wave function of the state, and G the Green's function $(E_i-H_0)^{-1}$ for the unperturbed Hamiltonian, with ψ_0 projected out. Similar inhomogeneous Schrödinger equations apply when the left-hand side is frequency dependent. We will make the assumption that E_1 vanishes in the following, although it is not difficult to correct the results for cases where this is not so. This also implies that we may treat operators of the form H_0-W, where W is an unspecified number, as though they may be inverted, although it is obviously possible to correct for those cases where W is an eigenvalue of H_0. The assumption of invertibility makes the discussion less awkward.

For cases where Eq. (2a) cannot be solved directly, or where one wishes to avoid doing so, a variational approach may be utilized.[4] Let ψ_T be a trial function. Then E_2 is given approximately by E_{2v}, where

$$E_{2v}=2(\psi_T^*H'\psi_0)+(\psi_T^*(H_0-E_i)\psi_T)\ .\tag{3}$$

If one should guess a ψ_T that turns out to be the exact ψ_1, $E_{2v}=E_2$. If $|i\rangle$ is the ground state of the system, Eq. (3) yields an upper bound for E_2. One may derive Eq. (3) directly from the Rayleigh-Ritz principle by assuming that ψ_0 is known exactly, expanding in a power series in the interaction and retaining terms through second-order in the perturbation, or directly through the variational principle for the Green's function

$$G=2G_T+G_T(H_0-E_i)G_T+O(\Delta G)^2\ ,\tag{4}$$

where $G=(E_i-H_0)^{-1}$, G_T a trial Green's function, and ΔG the difference between them.

For future reference, we review the derivation of Eq. (4). Using the definition of G, $G=G+G_T(H_0-E_i)G+G_T$. Manipulating the operators,

$$\begin{aligned}G&=2G_T+\Delta G+G_T(H_0-E_i)G_T+G_T(H_0-E_i)\Delta G\\&=2G_T+G_T(H_0-E_i)G_T+\Delta G\\&\quad+G(H_0-E_i)\Delta G-\Delta G(H_0-E_i)\Delta G\\&=2G_T+G_T(H_0-E_i)G_T-\Delta G(H_0-E_i)\Delta G\ .\end{aligned}$$

If E_i is the ground-state energy, then $\Delta G(H_0-E_i)\Delta G$ is a positive semidefinite operator, so that $2G_T+G_T(H_0-E_i)G_T$ is an upper bound on G. (We apply terms like "positive semidefinite" for operators in the sense that all expectation values are ≥ 0. Thus it is meaningful to speak of bounds for operators.)

We assume now that H_0 is an independent-particle Hamiltonian for a system of two or more bodies. For simplicity of discussion, assume a two-body system, with $H_0 = h_1 + h_2$, where h_i is a Hamiltonian for particle i. Clearly; h_1 commutes with h_2. We will use latin letters to denote many-body energies, and greek letters for single-particle energies. If H' is a single-particle operator for atoms, then Eq. (2a) is readily solvable in closed form for certain simple operators (typically multipole potentials) and hydrogenic unperturbed functions,[2] and by numerical techniques otherwise. The problem is much more difficult for perturbations in the form of two-particle operators, although considerable progress has been made, both by variational methods[5,6] and by direct solutions.[7,8]

A popular way of reducing the two-particle problem to an integral over single-particle solutions is via the identity[9]

$$(a+b)^{-1} = 2(\pi)^{-1} \int_0^\infty \frac{ab\,d\tau}{(a^2+\tau^2)(b^2+\tau^2)} \ . \tag{5}$$

Variational procedures are particularly attractive here,[10] even when the appropriate differential equations may be solved in closed form since the latter typically are expressed in terms of hypergeometric functions,[11] making the integrals difficult to evaluate.

As we have commented, the direct application of Eq. (3) yields an upper bound on E_2 if $|i\rangle$ is the ground state of the system. It would be very desirable to complement this with a lower bound of comparable accuracy and utility, and we proceed to do so.

The fundamental difficulty in solving Eq. (2) for a two-particle operator is that one cannot, even by resolving the problem into angular momentum components, reduce the problem to a finite set of ordinary differential equations. Reduction to ordinary differential equations comes at the price of the extra integration mandated by Eq. (5).

To ease the impact of this lack of separability forms part of the motivation for the present work. We proceeed by partitioning the problem into separable and nonseparable segments, with the former solved exactly and the latter treated by variational approximations similar to those used in earlier work.[9,10] The details of the construction of the method lead to the bound opposite to that customarily obtained.

We will start with the Green's function, with $E_i = \epsilon_1 + \epsilon_2$, where ϵ_1, ϵ_2 are the single-particle energies of state $|i\rangle$. The Green's function for two particles (noninteracting in the unperturbed problem) may be written

$$G = (E_i - H_0)^{-1} = [(\epsilon_1 - h_1) + (\epsilon_2 - h_2)]^{-1} \ , \tag{6}$$

where

$$E_i = \epsilon_1 + \epsilon_2 \ , \quad H_0 = h_1 + h_2 \ .$$

G satisfies the identity

$$\begin{aligned} G = \tfrac{1}{4}\{ & (\epsilon_1 - h_1)^{-1} + (\epsilon_2 - h_2)^{-1} \\ & - [(\epsilon_1 - h_1)^{-1} - (\epsilon_2 - h_2)^{-1}]^2 \\ & \times [(\epsilon_1 - h_1)^{-1} + (\epsilon_2 - h_2)^{-1}]^{-1}\} \ , \end{aligned} \tag{7}$$

where we have implicity assumed that one may also invert the single-particle Green's functions. Equation (7) is a consequence of the identity

$$(a+b)^{-1} = \tfrac{1}{4}[a^{-1} + b^{-1} - (a^{-1} + b^{-1}) + 4(a+b)^{-1}] \ .$$

Thus

$$\begin{aligned} (a+b)^{-1} &= \tfrac{1}{4}\{a^{-1} + b^{-1} - [(a+b)/ab - 4(a+b)^{-1}]\} \\ &= \tfrac{1}{4}\{a^{-1} + b^{-1} - [(a+b)^2 - 4ab]/ab(a+b)\} \\ &= \tfrac{1}{4}[a^{-1} + b^{-1} - (a-b)^2/\,ab(a+b)] \\ &= \tfrac{1}{4}[a^{-1} + b^{-1} - ab(a-b)^2/a^2b^2(a+b)] \\ &= \tfrac{1}{4}[a^{-1} + b^{-1} - (1/a - 1/b)^2/(1/a + 1/b)] \ . \end{aligned}$$

While Eq. (7) looks substantially more formidable than the original Green's function, it proves to be no more difficult to use in a variational principle than Eq. (4), and simple expressions, entirely analogous to those obtained from Eq. (3), result.

The first term in Eq. (7) is a sum of one-particle Green's functions, which may be evaluated exactly in hydrogenic problems,[12-14] and numerically elsewhere. [It generally proves unnecessary to actually compute these one-particle Green's functions anyway—one usually needs only to solve single-particle forms of Eq. (2a).] In the second term, the factor involving $[(\epsilon_1 - h_1)^{-1} - (\epsilon_2 - h_2)^{-1}]^2$ may be similarly calculated. The difficulty lies with the factor $[(\epsilon_1 - h_1)^{-1} + (\epsilon_2 - h_2)^{-1}]^{-1}$, and it is here that we resort to approximation, variational or otherwise. The variational approximations which one makes are not more difficult to apply than in the standard problem of Eq. (3), and are of comparable accuracy.

We note that if ϵ_1, ϵ_2 are the single-particle ground-state energies, the term

$$G_m = \tfrac{1}{4}[(\epsilon_1 - h_1)^{-1} + (\epsilon_2 - h_2)^{-1}] \tag{8}$$

is itself a lower bound on the two-particle Green's function G, since

$$G_p = G - G_m = \frac{[(\epsilon_1 - h_1)^{-1} - (\epsilon_2 - h_2)^{-1}]^2}{(\epsilon_1 - h_1)^{-1} + (\epsilon_2 - h_2)^{-1}}$$

is negative semidefinite. An improved lower bound may be immediately written, without doing much additional work, by replacing h_1, h_2 in the factor $[(\epsilon_1 - h_1)^{-1} + (\epsilon_2 - h_2)^{-1}]^{-1}$ in Eq. (7) by c numbers α_1, α_2, which are the single-particle energies of the lowest excited states contributing to G_p. (Note that not all excited states contribute to G_p. By construction, levels in which the excitation energy is shared equally between the particles have a null effect on this term.) A systematic improvement results when we construct a variational principle for $\tilde{G} = [(\epsilon_1 - h_1)^{-1} + (\epsilon_2 - h_2)^{-1}]^{-1}$, entirely analogous to Eq. (4). Thus

$$\tilde{G} \simeq \tilde{G}_v = 2\tilde{G}_T + \tilde{G}_T[(h_1 - \epsilon_1)^{-1} + (h_2 - \epsilon_2)^{-1}]\tilde{G}_T . \qquad (9)$$

Again, if the ϵ_i refer to single-particle ground states, $\tilde{G}_v$ is an upper bound on $\tilde{G}$.

The second-order correction to the energy becomes $E_2 = E_m - E_p$, where

$$E_m = \tfrac{1}{4}\langle\psi_0^* H'[(\epsilon_1 - h_1)^{-1} + (\epsilon_2 - h_2)^{-1}]H'\psi_0\rangle \qquad (10)$$

is calculated without approximation, and where

$$\begin{aligned} E_p = \tfrac{1}{4}\langle\psi_0^* H'&[(\epsilon_1 - h_1)^{-1} - (\epsilon_2 - h_2)^{-1}] \\ &\times[(\epsilon_1 - h_1)^{-1} + (\epsilon_2 - h_2)^{-1}]^{-1} \\ &\times[(\epsilon_1 - h_1)^{-1} - (\epsilon_1 - h_2)^{-1}]H'\psi_0\rangle \end{aligned} \qquad (11)$$

is determined approximately from the variational principle

$$\begin{aligned} E_p \simeq E_{pv} &= 2(\psi_T^* \tilde{H}'\psi_0) \\ &+ \langle\psi_T^*[(h_1 - \epsilon_1)^{-1} + (h_2 - \epsilon_2)^{-1}]\psi_T\rangle , \end{aligned} \qquad (12)$$

which is analogous in form to Eq. (3). The variational principle for $\tilde{G}$, Eq. (9), is used to construct Eq. (12), where the effective operator $\tilde{H}'$ is given by

$$\tilde{H}' = [(\epsilon_1 - h_1)^{-1} - (\epsilon_2 - h_2)^{-1}]H' . \qquad (13)$$

For the ground state, Eq. (12) gives an upper bound for E_p, so that what we have obtained is a lower bound for E_2.

No approximations were made in obtaining the preceding result, so that we have a rigorous lower bound for E_2. The real question is how useful the procedure is. To the end of determining this, we have applied the method to a simple physical problem that has been much studied in the literature, the calculation of C_6, the coefficient of $1/R^6$ in the Van der Waals interaction between two hydrogen atoms in their 1s states. In this case, using atomic units,

$$H' = [\vec{r}_1 \cdot \vec{r}_2 - 3(\vec{r}_1 \cdot \hat{n})(\vec{r}_2 \cdot \hat{n})]/R^3 ,$$

where $\vec{r}_1$ is the radius vector for an electron with respect to its "own" nucleus, $\vec{R}$ is the internuclear radius vector, and $\hat{n}$ a unit vector along $\vec{R}$. C_6 is given in second-order perturbation theory, and since both unperturbed atoms are spherically symmetric, the expression for C_6 reduces to $C_6 = 6E_2$, where E_2 is to be calculated for a perturbation $z_1 z_2$. One may write explicit expressions for all the functions that are needed to solve the problem.

$$\psi_0 = e^{-(r_1 + r_2)}/\pi , \qquad (14)$$

$$H'\psi_0 = r_1 r_2 \cos\theta_1 \cos\theta_2\, e^{-(r_1 + r_2)}/\pi , \qquad (15)$$

$$\tilde{H}'\psi_0 = r_1 r_2 (r_1 - r_2) \cos\theta_1 \cos\theta_2\, e^{-(r_1 + r_2)}/2\pi . \qquad (16)$$

We choose a trial function for Eq. (12) of the form

$$\psi_T = \cos\theta_1 \cos\theta_2\, e^{-(r_1 + r_2)} \sum \frac{a_i (r_1^{K_i} r_2^{J_i} - r_1^{J_i} r_2^{K_i})}{4\pi} , \qquad (17)$$

where a_i is an adjustable parameter. To evaluate the term $\langle\psi_T(h_1 - \epsilon_1)^{-1} + (h_2 - \epsilon_2)^{-1}\psi_T\rangle$ we require

$$[(h_1 - \epsilon_1)^{-1} + (h_2 - \epsilon_2)^{-1}]\psi_T = (4\pi)^{-1} \cos\theta_1 \cos\theta_2\, e^{-(r_1 + r_2)} \left(\sum_i a_i \sum_{L=1}^{K_i+1} (r_1^L r_2^{J_i} - r_2^L r_1^{J_i}) b_{LK_i} + \sum_{L=1}^{J_i+1} (r_1^{K_i} r_2^L - r_1^L r_2^{K_i}) \right), \qquad (18)$$

where the b_{Lp} are coefficients determined from

$$r_1^q e^{-r_1} \cos\theta_1 = (h_1 - \epsilon_1)\phi_q \cos\theta_1 ,$$

with $\phi_q = \sum_{L=1}^{q+1} b_{Lq} r_1^L e^{-r_1}$. Here $b_{Lq+1} = (q+1)^{-1}$, $b_{Lp} = [p(p+1) - 2]/2p b_{Lp+1}$. Integrating over angles and combining terms, we reduce to sums of products of Γ functions:

$$\begin{aligned} E_p \simeq E_{pv} = \tfrac{1}{9} \Bigg\{ & 8 \sum_i a_i \frac{(K_i + 2)!(J_i + 2)!(K_i - J_i)}{2^{K_i + J_i + 7}} + 2 \sum_i \sum_m a_i a_m \\ & \times \left(\sum_{L=2}^{K_m+1} b_{LK_m} \frac{(L + K_i)!\,(J_m + J_i)! - (J_i + L)!(K_i + J_m)!}{2^{L + K_i + J_i + J_m + 2}} \right. \\ & \left. + \sum_{L=2}^{J_m+1} b_{LJ_m} \frac{(K_i + K_m)!(J_i + J_L)! - (L + K_i)!(J_i + K_m)!}{2^{K_i + K_m + L + J_i + 2}} \right) \Bigg\} . \end{aligned} \qquad (19)$$

TABLE I. Bounds on C_6 for H – H. V denotes variational, PA denotes Padé approximant. Number (s) in parentheses indicate number(s) of parameters that characterize calculation.

Lower bounds		Upper bounds	
-6.75^{a}	(V-0)	-6.000^{c}	(V-1)
-6.56^{b}	(V-1)	-6.482^{c}	(V-3)
-6.515^{b}	(V-2)	$-6.498\,4^{c}$	(V-6)
-6.509^{b}	(V-3)	$-6.499\,002\,5^{c}$	(V-10)
$-6.499\,150^{b}$	(V-4)	$-6.499\,023\,0^{c}$	(V-11)
$-6.499\,137^{b}$	(V-5)	$-6.499\,025\,2^{c}$	(V-12)
$-6.499\,056^{b}$	(V-6)	$-6.499\,026\,0^{c}$	(V-13)
$-6.499\,035^{b}$	(V-7)	-6.249^{d}	(PA-[1, 0])
-6.780^{d}	(PA-[1, 1])	-6.470^{d}	(PA-[2, 1])
-6.542^{d}	(PA-[2, 2])	-6.493^{d}	(PA-[3, 2])
-6.517^{d}	(PA-[3, 3])	-6.497^{d}	(PA-[4, 3])
-6.499^{d}	(PA-[4, 4])	-6.498^{d}	(PA-[5, 4])
-6.499^{d}	(PA-[5, 5])	-6.499^{d}	(PA-[6, 5])
-6.499^{d}	(PA-[6, 6])	-6.499^{d}	(PA-[7, 6])
-6.499^{d}	(PA-[7, 7])	-6.486^{e}	(PA-[2, 1])
-6.509^{e}	(PA-[2, 2])		

[a] This work, E_m only.
[b] This work.
[c] Reference 16.
[d] Reference 15.
[e] Reference 9.

To evaluate E_m, we must solve the equation

$$[(h_1-\epsilon_1)^{-1}+(h_2-\epsilon_2)^{-1}]z_1z_2\psi_0=\phi\,. \tag{20}$$

Using the recursion relations following Eq. (18), this yields the result $C_m=6E_m=-6.75$ a.u., already a reasonable approximation for the accepted value, which, to three significant figures, is -6.50. Using Eq. (9), with α_1, α_2 corresponding to an excitation of one atom to the $2p$ and the other to the $3p$ state, we obtain a lower bound $C_6=-6.57$, which is close to the -6.56 which results from a one-parameter trial function in Eq. (18). The variational lower bound may be systematically improved by enlarging the number of adjustable parameters. We summarize our results in Table I, which also includes the results of other authors.[9,10,15-17]

Our results should be compared to the accurate variational upper bound computed by Hirschfelder and Löwdin (HL),[16] who used up to 13 parameters in a trial function drawn from a single-particle basis set similar to ours. It appears that the accuracy which we achieve with 6 or 7 parameters is comparable to that achieved in their calculation with 13 parameters. (Furthermore, they experimented with different choices of basis functions, while we merely systematically extended our set as the number of parameters was increased.) This stems in part from the fact that HL are calculating the entire perturbation energy, while our variational approximation provides an estimate of E_p, which is only 4% of the full value. Hence we may tolerate a fractional error 25 times larger for a given overall accuracy.

That E_m alone is already quite a good approximation may be peculiar to the present problem, but physical considerations lead one to believe that it is of much greater generality. E_m includes excitations to all states of the system. The contributions to E_2 from levels where the excitation energy is shared equally between the two particles are included exactly in the E_m term; the contribution of E_p to E_2 vanishes for these states. Thus E_m overestimates the absolute value of the contribution of E_2 arising only from levels where the excitation energy is shared unequally between the electrons, and the role of E_p is to correct for this. The variational procedure underestimates the magnitude of this correction. Since the dominant contributions to E_2 tend to arise from the equal and nearly equal excitation states, the error is restricted to terms which are *a priori* of lesser importance.

Had we chosen to do so, E_p could have been evaluated by a convolution method similar to Eq. (5) since $(1/a+1/b)^{-1}=ab/(a+b)$.

The technique of Padé approximants has been used to determine upper and lower bounds on C_6.[9,15] In a number of cases, very close correspondence exists between a Padé lower bound and our lower bound for a comparable number of adjustable parameters or the Padé equivalent. This may reflect the use in the latter case of exact values of scalar sum rules $S(k)$, several of which may be generated exactly in a variational calculation[18] with the single-particle functions that characterize our basis set.

To summarize, we have discovered a new variational principle for two-particle perturbation energies, which is neither more difficult to apply than older methods nor does it appear to converge more slowly. In addition, for calculations involving the ground state, it supplies a rigorous (and apparently accurate) lower bound for E_2 in contrast to the existing principle of variational perturbation theory, which gives an upper bound.

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