

Upper bounds for the ground-state second-order Perturbation Theory

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A family of upper bounds for the ground-state second-order energy, derived from the Perturbation Theory, has been obtained. The bounds have been evaluated for the static electric dipole polarizability of the hydrogen atom.

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'n Versameling van boonste perke vir die grondtoestand tweede-orde energie, wat afgelei is uit die sturingsteorie, is verkry. Die perke vir die statiese elektriese dipoolpolariseerbaarheid van die waterstofatoom is geëvalueer.

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It is often impossible to obtain the complete set of eigenfunctions of the zero'th-order Hamiltonian, which is required for the more usual forms of application of the Perturbation Theory (PT). This, in turn, makes it impossible to apply exact corrections to the zero'th-order energy of the system and its wave functions.

This latter situation has led to the publication of many papers which attempt to approximate these correction energies. The main interest has been in second-order corrections.¹⁻³ The different formulations that appear in the current literature make use of a discrete set of eigenfunctions of H_0 , or its eigenvalues.

In this paper we examine the possibility of developing an alternative formulation. In principle, this formulation would allow us to obtain upper bounds for the second-order perturbation energy, expressed only in terms of the ground-state wave function. These bounds can be improved by adding a discrete set of excited-state wave functions.

General theory

In the Rayleigh-Schrödinger PT, the ground-state second-order energy is expressed as

$$E^{(2)} = \langle \varphi_0^0 | VR_0V | \varphi_0^0 \rangle, \quad (1)$$

where V is a perturbation operator, φ_0^0 is the eigenfunction of the zero'th-order Hamiltonian for the ground state, and R_0 is the reduced resolvent, whose spectral resolution is defined as

$$R_0 = \sum_{k=1}^{\infty} \frac{O_k^0}{E_0^0 - E_k^0}, \quad (2)$$

where O_k^0 is the projector associated to the eigenfunction φ_k^0 . From eq. (2), we have

$$R_0 \leq 0 \quad \text{and} \quad VR_0V \leq 0. \quad (3)$$

Let A and B be two arbitrary operators which usually do not commute. For the inverse of $(A-B)$, we have the following identity, valid for the so-called right inverse:⁴

$$(A-B)^{-1} = A^{-1} + (A-B)^{-1}BA^{-1}. \quad (4)$$

By repeated use of eq. (4), one may derive the expansion

$$(A-B)^{-1} = \sum_{s=0}^{n-1} (A^{-1}B)^s A^{-1} + (A-B)^{-1} (BA^{-1})^n, \quad (5)$$

with $n=1, 2, 3, \dots$

This expression is totally different to those found in the literature.^{5,6} It can be considered as a generalization of eq. (A4) of ref. 5, or eq. (87) of ref. 6.

If we apply this expansion to operator $(E_0^0 - H_0)^{-1}$, we obtain the particular form,

$$(E_0^0 - H_0)^{-1} = \sum_{s=0}^{n-1} (H_0)^s (E_0^0)^{-s-1} + (E_0^0)^{-n} (H_0)^n (E_0^0 - H_0)^{-1}. \quad (6)$$

Inserting eq. (6) into eq. (2), and making use of the spectral decomposition of H_0 , we obtain

$$R_0 = \sum_{s=0}^{n-1} (H_0)^s (E_0^0)^{-s-1} - n O_0^0 (E_0^0)^{-1} + \sum_{k=1}^{\infty} \left(\frac{E_k^0}{E_0^0} \right)^n \frac{O_k^0}{E_0^0 - E_k^0}. \quad (7)$$

We can also obtain the same results by employing the expansion for the left inverse or the symmetric expansion.⁷

Upper bounds to $E^{(2)}$

Let us consider the last term of the right-hand side of eq. (7). It obeys the inequality (see Results and Discussion),

$$\sum_{k=1}^{\infty} \left(\frac{E_k^0}{E_0^0} \right)^n \frac{O_k^0}{E_0^0 - E_k^0} < 0, \quad (8)$$

and we may write the following upper bound to R_0 :

$$R_0 < \sum_{s=0}^{n-1} (H_0)^s (E_0^0)^{-s-1} - n O_0^0 (E_0^0)^{-1}. \quad (9)$$

We can improve eq. (9) by considering one part of the rejected term,

$$R_0 < \sum_{s=0}^{n-1} (H_0)^s (E_0^0)^{-s-1} - n O_0^0 (E_0^0)^{-1} + \sum_{k=1}^p \left(\frac{E_k^0}{E_0^0} \right)^n \frac{O_k^0}{E_0^0 - E_k^0}, \quad (10)$$

where p means a finite sum.

Having in mind these considerations, we write the upper bound to $E^{(2)}$ as

$$E^{(2)} < \sum_{s=0}^{n-1} \frac{\langle \varphi_0^0 | V (H_0)^s V | \varphi_0^0 \rangle}{(E_0^0)^{s+1}} - \frac{n \langle \varphi_0^0 | V | \varphi_0^0 \rangle}{E_0^0} + \sum_{k=1}^p \left(\frac{E_k^0}{E_0^0} \right)^n \frac{|\langle \varphi_0^0 | V | \varphi_k^0 \rangle|^2}{E_0^0 - E_k^0}. \quad (11)$$

We will call the terms obtained in eq. (11) with $n=1$ and varying p , 'the first family', with $n=2$ and varying p , 'the second family', and so on. Each family is composed of

'members' which are obtained by varying p . For example, if we have $n=2$ and $p=4$, we will say that we are dealing with the fourth member of the second family.

Results and Discussion

Following our traditional line of investigation, we shall apply this method to the calculation of lower bounds to the static electric dipole polarizability (SEDP) of the hydrogen atom. The passage, from the upper bound to $E^{(2)}$ to the SEDP lower bound, is direct.⁸ In the case of the hydrogen atom, we have

$$\alpha(\mu, \mu) > -2 \sum_{s=0}^{n-1} \frac{\langle \varphi_0^0 | \mu (H_0)^s \mu | \varphi_0^0 \rangle}{(E_0^0)^{s+1}} - 2 \sum_{k=1}^p \left(\frac{E_k^0}{E_0^0} \right)^n \frac{|\langle \varphi_0^0 | \mu | \varphi_k^0 \rangle|^2}{E_0^0 - E_k^0}, \quad (12)$$

where $\alpha_0(\mu, \mu)$ is the μ -component of the polarizability tensor, $\vec{\mu}$ is the μ -component of the dipole moment operator \vec{M} , and φ_k^0 is the eigenfunction of the k -state.

We have calculated the scalar polarizability:

$$\alpha_0 = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}). \quad (13)$$

The results are shown in Table 1 for $n=1, 2$, and 3. The index p in the table refers to eq. (12).

Table 1 Lower bounds for the SEDP of the hydrogen atom

p	Lower bound (a.u.)		
	$n=1$	$n=2$	$n=3$
0	4,000	4,000	-5,333
1	4,138	4,034	-5,324
2	4,162	4,037	-5,324
3	4,164	4,037	-5,324

Other lower bounds for the SEDP of the hydrogen atom reported are 4,125,⁹ 4,000, 4,3162, 4,3800,^{10,11} and 4,5 a.u.¹² The exact value is 4,5 a.u. We can see that this method provides good lower bounds for the SEDP with $n=1$ and varying p . The reasons are that

- the results show that the first family has a more rapid convergence to the exact value; and
- the calculation of matrix elements in the first family is very easy by comparison with that for the other families.

The choice of p is determined by the results of the calculation. When we find that there is no significant change in the value of two consecutive terms in one family, we terminate the calculation.

There are two comments in the case of large values of n :

- In the case of polyelectronic atoms or molecules, the difficulties that appear in the evaluation of most of the matrix elements, having the form $\langle \mu (H_0)^n \mu \rangle$, can be avoided by using the rules of commutation between H_0 and \vec{M} .

(ii) In the fourth and following families, there appear divergent integrals which make the calculations difficult.

The table reveals that, when the value of n rises, the lower bounds begin to differ more and more from the experimental values for the polarizabilities. This should indicate that the best values for the lower bounds will be obtained with $n=1$ or 2. Accordingly, the second comment above becomes a hypothetical problem.

Equation (11) has certain limitations which arise from inequality (8). It holds only when (E_k^0/E_0^0) is positive. However, it is possible to define a similar expansion to eq. (5), replacing n by $2n$, thereby giving a rigorous sense to the inequality (8). In the case of the hydrogen atom, this expression is accurate because the discrete energy spectra contain only negative values.

References

- 1 B.L. Burrows, *J. Phys. B*, 1974, 7, 881.
- 2 J. Killingbeck, *J. Phys. B*, 1975, 8, 1987.
- 3 I. Shimamura, *J. Phys. B*, 1975, 8, 52.
- 4 P.O. Löwdin, *J. Math. Phys.*, 1968, 6, 1341.
- 5 P.O. Löwdin, *J. Math. Phys.*, 1962, 3, 969.
- 6 P.O. Löwdin, *Phys. Rev.*, 1965, 139, A357.
- 7 P.O. Löwdin in 'Perturbation Theory and its Applications in Quantum Mechanics' (C.H. Wilcox, ed.), John Wiley & Sons Inc., New York, 1966, p.273.
- 8 P.W. Atkins, 'Molecular Quantum Mechanics', Vol II, Clarendon Press, Oxford, 1970, p.402.
- 9 O. Goscinski, *Int. J. Quantum Chem.*, 1968, 2, 761.
- 10 T. Yamabe, K. Tanaka, S. Ishimaru, and K. Fukui, *Bull. Chem. Soc. Jpn.*, 1974, 47, 1578.
- 11 J. Goodisman, *J. Chem. Phys.*, 1967, 47, 2707.
- 12 P. Lindner and P.O. Löwdin, *Int. J. Quantum Chem.*, 1968, 2S, 161.