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WAVE OPERATOR PERTURBATION THEORY
FOR INTERMOLECULAR INTERACTIONS
A TEST ON H$_2^+$

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The first-order function and the second-order energy of a perturbation theory proposed by the present author are evaluated for H$_2^+$ by means of a Hylleraas variation principle adapted to this theory. It is found that thus a considerable improvement of the wave function and the energy respectively is obtained. The importance of second-order exchange forces is observed. The Unsold approximation for the second-order energy is tested.

Formulating a perturbation method to calculate intermolecular interactions leads to specific difficulties, e.g., an eigenfunction of the unperturbed operator, $H_0$, which is the sum of the molecular operators, is a very poor starting function for the perturbation theory, as it does not have the desired symmetry properties; the symmetrized product of molecular eigenfunctions is not an eigenfunction of $H_0$.

A way of dealing with these difficulties is application of the wave operator theory as modified by the present author for the case of intermolecular interactions [1,2]. This theory starts from the symmetrized product of molecular or atomic functions - the zero-order energy being the sum of molecular or atomic energies - and yields successive corrections to the wave function and the binding energy of the complex as terms in a perturbation series. All perturbed functions are orthogonal to the starting function and have the proper symmetry.

To test this theory it is applied to the simplest case of interatomic interactions: the lowest two states of H$_2^+$. The unperturbed function is given as

$$\psi_0 = A \phi_0 ,$$

where $\phi_0 = 1s_a(1) = \pi^{-\frac{1}{2}} \exp(-r_a)$, $A = \frac{1}{2}(I \pm P_{ab})$, + for the 1$\sigma_g$ state, - for the 1$\sigma_u$ state.

The first-order interaction energy

$$\epsilon_1 = \frac{\langle \phi_0 | AV | \phi_0 \rangle}{\langle \phi_0 | A \phi_0 \rangle}$$

with

$$V = \frac{1}{R_{ab}} - \frac{1}{r_{b1}} \left( H_0 \frac{\Delta_1}{2} - \frac{1}{r_{a1}} \right) ,$$

which is also the result of a molecular orbital calculation with $\psi_{M.O.} = 1s_a(1) \pm 1s_b(1)$, is easily evaluated.

The second-order energy

$$\epsilon_2 = \frac{\langle \phi_0 | VP R_0 P V | \phi_0 \rangle}{\langle \phi_0 | A \phi_0 \rangle} ,$$

where

$$P = A - \frac{A \phi_0 \langle \phi_0 | A \phi_0 \rangle}{\langle \phi_0 | A | \phi_0 \rangle} \quad \text{and} \quad R_0 = \sum_{k \neq 0} \frac{|\phi_k \rangle \langle \phi_k |}{E_k - E_0} \ |

(\phi_0$ and all $\phi_k$ are eigenfunctions of $H_0$), can be approximated to any required degree of accuracy by a modified Hylleraas variation principle [3] (see also [4]). Assume an arbitrary function $\phi$ and consider the functional

$$W = \frac{1}{\langle \phi_0 | A | \phi_0 \rangle} \times$$

$$\times \left[ \langle \phi | H_0 - E_0 | \phi \rangle + \langle \phi | PV \phi_0 \rangle + \langle PV \phi_0 | \phi \rangle \right] .$$

It is proved, substituting $\phi = R_0 PV \phi_0 + \delta$, that
### Table 1
1$d_g^*$-state

<table>
<thead>
<tr>
<th>$R$ (a.u.)</th>
<th>$\tilde{\epsilon}_2$ (a.u.)</th>
<th>$\tilde{E} - E_0$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n_{\text{max}} = 2$</td>
<td>(2)</td>
</tr>
<tr>
<td>0.5</td>
<td>-0.3347 -0.3468 -0.3510 -0.3528 -0.3336 -0.3541</td>
<td>0.8620 0.8988 0.8906 0.8873 0.8847 0.8720</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.1646 -0.1878 -0.1921 -0.1933 -0.1941 -0.1946</td>
<td>0.0753 0.1131 0.1034 0.1012 0.1001 0.0993</td>
</tr>
<tr>
<td>1.5</td>
<td>-0.0767 -0.0981 -0.1005 -0.1018 -0.1025 -0.1029</td>
<td>-0.0729 -0.0555 -0.0595 -0.0609 -0.0618 -0.0622</td>
</tr>
<tr>
<td>2.0</td>
<td>-0.0363 -0.0512 -0.0534 -0.0546 -0.0551 -0.0553</td>
<td>-0.0962 -0.0928 -0.0932 -0.0944 -0.0948 -0.0950</td>
</tr>
<tr>
<td>2.5</td>
<td>-0.0183 -0.0271 -0.0298 -0.0306 -0.0309 -0.0311</td>
<td>-0.0884 -0.0900 -0.0897 -0.0906 -0.0908 -0.0910</td>
</tr>
<tr>
<td>3.0</td>
<td>-0.0104 -0.0148 -0.0177 -0.0182 -0.0185 -0.0186</td>
<td>-0.0733 -0.0754 -0.0757 -0.0761 -0.0763 -0.0764</td>
</tr>
<tr>
<td>3.5</td>
<td>-0.0068 -0.0087 -0.0112 -0.0117 -0.0119 -0.0120</td>
<td>-0.0576 -0.0590 -0.0598 -0.0600 -0.0602 -0.0603</td>
</tr>
<tr>
<td>4.0</td>
<td>-0.00491 -0.00569 -0.00744 -0.00796 -0.00817 -0.00823</td>
<td>-0.0437 -0.0455 -0.0453 -0.0454 -0.0456 -0.0457</td>
</tr>
<tr>
<td>5.0</td>
<td>-0.00267 -0.00308 -0.00356 -0.00406 -0.00418 -0.00425</td>
<td>-0.0230 -0.0235 -0.0238 -0.0240 -0.0241 -0.0241</td>
</tr>
<tr>
<td>6.0</td>
<td>-0.00136 -0.00174 -0.00182 -0.00204 -0.00218 -0.00222</td>
<td>-0.01103 -0.0244 -0.01153 -0.01163 -0.01171 -0.01176</td>
</tr>
<tr>
<td>7.0</td>
<td>-0.00067 -0.00092 -0.00096 -0.00101 -0.00111 -0.00115</td>
<td>-0.00502 -0.00530 -0.00535 -0.00537 -0.00542 -0.00546</td>
</tr>
</tbody>
</table>

### Table 2
1$d_u^*$-state

<table>
<thead>
<tr>
<th>$R$ (a.o.)</th>
<th>$\tilde{\epsilon}_2$ (a.u.)</th>
<th>$\tilde{E} - E_0$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n_{\text{max}} = 2$</td>
<td>(2)</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.0511 -0.0750 -0.0843 -0.0878 -0.0900 -0.0920</td>
<td>0.9665 0.9485 0.9423 0.9404 0.9397 0.9390</td>
</tr>
<tr>
<td>1.5</td>
<td>-0.0114 -0.0174 -0.0188 -0.0195 -0.0203 -0.0208</td>
<td>0.5546 0.5487 0.5475 0.5471 0.5466 0.5463</td>
</tr>
<tr>
<td>2.0</td>
<td>-0.00222 -0.00367 -0.00388 -0.00406 -0.00422 -0.00434</td>
<td>0.3357 0.3340 0.3337 0.3336 0.3335 0.3334</td>
</tr>
<tr>
<td>2.5</td>
<td>-0.00026 -0.00069 -0.00078 -0.00081 -0.00084 -0.00086</td>
<td>0.20896 0.20834 0.20824 0.20822 0.20819 0.20818</td>
</tr>
<tr>
<td>3.0</td>
<td>-0.00001 -0.00021 -0.00033 -0.00037 -0.00038 -0.00038</td>
<td>0.13241 0.13211 0.13201 0.13199 0.13198 0.13198</td>
</tr>
<tr>
<td>3.5</td>
<td>-0.00011 -0.00023 -0.00036 -0.00044 -0.00046 -0.00046</td>
<td>0.08487 0.08470 0.08459 0.08455 0.08453 0.08453</td>
</tr>
<tr>
<td>4.0</td>
<td>-0.00022 -0.00030 -0.00040 -0.00053 -0.00056 -0.00057</td>
<td>0.05478 0.05466 0.05458 0.05451 0.05449 0.05448</td>
</tr>
<tr>
<td>5.0</td>
<td>-0.00029 -0.00034 -0.00037 -0.00052 -0.00056 -0.00059</td>
<td>0.02298 0.02291 0.02289 0.02280 0.02277 0.02275</td>
</tr>
<tr>
<td>6.0</td>
<td>-0.00027 -0.00030 -0.00031 -0.00038 -0.00046 -0.00048</td>
<td>0.00957 0.00953 0.00952 0.00946 0.00943 0.00941</td>
</tr>
<tr>
<td>7.0</td>
<td>-0.00021 -0.00023 -0.00025 -0.00027 -0.00033 -0.00036</td>
<td>0.00390 0.00387 0.00385 0.00383 0.00380 0.00378</td>
</tr>
</tbody>
</table>
W \equiv \epsilon_2$, the equality sign only holding if $\varphi = R_0 PV \varphi_0 + \lambda \varphi_0$. Minimizing $W$ yields both an approximate second-order energy, $\tilde{\epsilon}_2$, and first-order function $\tilde{\psi}^{(1)} = P \varphi_{\text{min}} \approx \tilde{\psi}^{(1)} = PR_0 PV \varphi_0$.

In this calculation $\varphi$ is expanded as a linear combination of atomic orbitals of the form

$$\varphi_{nlm} = R_{nl}(r) Y_{l}^{m}(\theta, \varphi),$$

where

$$R_{nl}(r) = 2^{\frac{3}{2}} \frac{(n-l-1)!}{(n+l+1)!} (2r)^l L_{n+l-1}(2r) e^{-r},$$

$Y_{l}^{m}(\theta, \varphi)$ are spherical harmonics, and $L(2r)$ are associated Laguerre polynomials.

Compared with the hydrogen atomic eigenfunctions, these orbitals have the advantage that, without including continuum functions, they form a complete orthonormal set for bound functions [5,6].

$W$ is minimized with respect to variation of the expansion coefficients. It is verified that the approximate second-order energy indeed gives an improvement of the first-order result. The quality of the first-order function is checked by calculating the expectation value

$$\bar{E} = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

with the function $\psi = \psi_0 + \tilde{\psi}^{(1)} = A \varphi_0 + P \varphi_{\text{min}}$.

The results are compared with the very accurate calculations on $H_2$ by Bates et al. [7] and Peek [8].

The second-order energy can also be calculated in the Unsöld approximation [9].

The expression between square brackets is evaluated and compared with $\epsilon_2$ in order to compute $\Delta E_{\text{av}}$ as a function of the interatomic distance.

Calculations and results

The calculation of $\epsilon_1$, $\tilde{\epsilon}_2$ and $\bar{E}$ necessitates the computation of two centre one electron integrals, $\epsilon_1$ and $\tilde{\epsilon}_2$ only requiring the overlap and $1/r$ type and $\bar{E}$ moreover kinetic energy integrals.

These integrals were calculated on an IBM 7094 computer with a program made available to us by Prof. Richardson and Dr. Vaught of Purdue University, Indiana. This program expands the integrals in $A_n$ and $B_n$ integrals after a transformation to elliptical coordinates. Assembling the integrals as well as the minimizing procedure were performed on an IMB 1800 computer.

The calculation of the Unsöld second-order energy involves integrals of the overlap, $1/r$ and $1/r^2$ types. Of the two integrals of the latter type that occur,

$$\int \varphi_a(1) \varphi_b(1) \frac{d\tau_1}{r_{a1}^{-1} r_{b1}^{-1}}$$

is easily computed.
is expressed after some coordinate transformations in the functions
\[ E_1(x) = \int_{-\infty}^{\infty} e^{-\frac{x^2}{2}} \, d\tau_1 \]
\[ E_2(x) = \int_{-\infty}^{\infty} e^{-\frac{-x^2}{2}} \, d\tau_1 \quad (x > 0), \]
which are tabulated [11].

The results are given in tables 1-4.

Tables 1 and 2 show, respectively for the \(1\sigma_g\) and \(1\sigma_u\) state, \(\epsilon_2 = W_{\min}\) and \(E - E_0\) as a function of the size of the variational basis. In each basis \(n\) runs from 2 to \(n_{\text{max}}\) and \(l\) from 0 to \((n-1)\) (\(l\) smaller than 6). Functions with \(m \neq 0\) are excluded for symmetry reasons. With \(n_{\text{max}}\) the total number of variation functions is indicated between brackets.

It is seen that, indeed, \(\epsilon_2\) decreases with each enlargement of the basis. Moreover that, generally, \(E\) decreases too, which means that \(\psi_0 + \psi(1)\) becomes a better approximation to the exact wave function of the molecule.

In table 3, \(\epsilon_1\), \(\epsilon_1 + \epsilon_2\) and \(E - E_0\) are compared with the very accurate results of refs. [7,8]. This comparison is illustrated in fig. 1.

Table 4 gives \(\Delta E_{\text{av}}\) as a function of the interatomic distance.

Conclusions

In the ground state, where the first-order energy is a very poor approximation to the exact energy in all respects (equilibrium distance, dissociation energy, behaviour for large \(R\)), the second-order energy yields a reasonably good correction. Inclusion of the first-order function gives a considerable improvement in the expectation value of \(H\) (\(E_0 + \epsilon_1\) equals the expectation value of \(H\) with \(\psi_0\) only). Both \(\epsilon_1 + \epsilon_2\) and \(E - E_0\) are almost equal to the exact interaction energy for \(R > 3\alpha_0\). For the lowest anti-bonding state the first-order approximation is already rather good. The corrections given by the second-order energy and by the first-order function are indeed small and improve the results even more.

The importance of the second-order exchange energy is immediately seen, as, without exchange, the second-order correction would have the same magnitude for bonding and anti-bonding states.

Of the average excitation energy in the Unsöld approximation can only be said that it is high for interatomic distances in the chemical binding region and decreases with larger \(R\) to the magnitude of the atomic ionization energy.

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References