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Some investigations of the MP2-R12 method

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Summary. The MP2-R12 method was introduced by Kutzelnigg and Klopper to overcome the problem caused by truncation of the one electron basis set in correlation energy calculations at the Møller–Plesset second order level of approximation. Here, we have evaluated the integrals required by their simplest scheme using the Rys-quadrature procedure. Results are presented for Ne, H_2O, and HF using large *spdf* gaussian basis sets.

Key words: Electron correlation – Basis set limit

1. Introduction

In a series of papers [1–9], Kutzelnigg and Klopper (KK) have introduced a novel method to overcome the basis set deficiency in Møller–Plesset calculations of the correlation energy at the second order of perturbation theory. Readers are referred to this series of papers; here, we shall give only a brief summary of the ideas and aims of the method. Our purpose is to see whether this approach is a viable way of overcoming the enormous basis set problem of quantum chemistry.

KK commence with the Hylleraas variational principle for the MP2 pair energies. They argue that, in the usual finite one-electron basis approach, the main deficiency of the first order wavefunction ψ_1 is its failure to obey the cusp condition as the interelectronic distance r_{ij} tends to zero. They therefore consider a first order wavefunction for the ij pair constructed from the reference determinant with the spin orbitals ϕ_i and ϕ_j replaced by u_{ij}

$$u_{ij}(1,2) = \tfrac{1}{2}c_{ij}\{1 - P(1)\}\{1 - P(2)\}r_{12}[ij] + \sum d_{ij}^{ab}[ab] \tag{1}$$

where c_{ij} and d_{ij}^{ab} are linear variational parameters,

$$P(1) = \sum_k |\phi_k(1)\rangle\langle\phi_k(1)| \tag{2}$$

and

$$[pq] = \frac{1}{\sqrt{2}}\{\phi_p(1)\phi_q(2) - \phi_q(1)\phi_p(2)\}. \tag{3}$$

In our notation, $i, j, \ldots$ run over occupied orbitals, $a, b, \ldots$ run over virtual orbitals and $p, q, \ldots$ run over all orbitals. They substitute (1) into the Hylleraas expression for the ij pair energy

$$f_{ij} = 2\langle [ij] | \frac{1}{r_{ij}} | u_{ij}(1,2)\rangle + \langle u_{ij}(1,2) | F(1) + F(2) - \varepsilon_i - \varepsilon_j | u_{ij}(1,2)\rangle. \qquad (4)$$

An exact evaluation of (4) requires the evaluation of three electron integrals. KK evaluated (4) approximately using the assumptions that ϕ_i and ϕ_j are the exact eigenfunctions of the Fock operator F and that the orbital set $\{\phi_p\}$ is complete in one-electron space, i.e.

$$1 = \sum_p |\phi_p(1)\rangle\langle\phi_p(1)| \equiv Q(1). \qquad (5)$$

The result of inserting these assumptions into (4) is that the pair energy is a sum of two terms: the conventional MP2 pair energy e_{ij} and a term correcting for the incompleteness in two-electron space,

$$\sum_{k=1}^{3} \langle [ij] | r_{12}[1 - Q(1)Q(2)]A_k | [ij]\rangle \qquad (6)$$

where

$$A_1 = (c_{ij} - \tfrac{1}{2}c_{ij}^2)\frac{1}{r_{12}} \qquad (7a)$$

$$A_2 = -\tfrac{1}{4}c_{ij}^2 \frac{1}{r_{12}}(\mathbf{r}_{12} \cdot (\boldsymbol{\nabla}_1 - \boldsymbol{\nabla}_2)) \qquad (7b)$$

$$A_3 = -\tfrac{1}{4}c_{ij}^2[K(1) + K(2), r_{12}]. \qquad (7c)$$

A_3 involves a commutator with $K(1)$, the exchange operator in $F(1)$. The evaluation of the A_3 term in (6), involving three electron integrals, is much more difficult than the evaluation of the A_1 and A_2 terms. If A_3 is ignored then the pair energy f_{ij} is given by

$$f_{ij} = e_{ij} + (2c_{ij} - c_{ij}^2)V_{ij} + c_{ij}^2 U_{ij} \qquad (8)$$

where

$$V_{ij} = \tfrac{1}{2} - \tfrac{1}{2}\sum_{p<q} \langle [ij] | r_{12} | [pq]\rangle\langle [pq] | \frac{1}{r_{12}} | [ij]\rangle \qquad (9)$$

and

$$U_{ij} = \tfrac{3}{4} + \tfrac{1}{4}\sum_{p<q} \langle [ij] | r_{12} | [pq]\rangle\langle [pq] | \frac{1}{r_{12}}(\mathbf{r}_{12} \cdot (\boldsymbol{\nabla}_1 - \boldsymbol{\nabla}_2)) | [ij]\rangle. \qquad (10)$$

KK made the important points that (9) and (10) involve completeness relations such that V_{ij} and U_{ij} tend to zero as the one-electron basis set becomes complete.

In the atomic case, the MP2 partial wave expansion has increments $\sim(l + 1/2)^{-4}$ for each succeeding completed l-shell in the basis set. The term A_1 looks after this deficiency, and the terms A_2 and A_3 look after the $\sim(l + 1/2)^{-6}$ deficiency. Thus, if the terms A_1, A_2 and A_3 are computed, the partial wave expansion for the MP2-R12 method will have increments $\sim(l + 1/2)^{-8}$. KK suggest the commutator in (7c) may make its contribution less significant than that from the A_2 term, and that it may therefore be reasonable to ignore A_3. All calculations published to date by KK have excluded the term A_3, although it has been included in forthcoming calculations [7–9]. We ignore A_3, as its full evaluation requires three electron integrals.

By ignoring this term, the MP2-R12 method has increments $\sim(l+1/2)^{-6}$. It has been known for a long time [10–12] that the lack of the correlation cusp in the first order wavefunction is the reason for the slow convergence of the MP2 (or any CI method) with respect to basis set, and this manifests itself in the $(l+1/2)^{-4}$ convergence.

The final step in the KK procedure is to optimise f_{ij} with respect to c_{ij} to yield

$$f_{ij} = e_{ij} + c_{ij} V_{ij} \tag{11}$$

where

$$c_{ij} = \frac{V_{ij}}{(V_{ij} - U_{ij})}. \tag{12}$$

This is a stable procedure, because it turns out that V_{ij} and U_{ij} have opposite signs, at least for the cases considered so far.

Our purpose in this work is not to present any new theory or approximations, but to give some independent calculations using this procedure and discuss the likely contribution of this novel approach to the basis set problem in quantum chemistry. Before we can proceed with these calculations two new forms of gaussian integrals need to be evaluated:

$$(pq|r_{12}|rs) = \int\int \psi_p(1)\psi_q(1) r_{12} \psi_r(2)\psi_s(2)\, d\tau_1\, d\tau_2 \tag{13}$$

and

$$\begin{aligned}\langle pr|\frac{1}{r_{12}}(\mathbf{r}_{12}\cdot(\nabla_1-\nabla_2))|qs\rangle &= \int\int \psi_p(1)\psi_r(2)\frac{\mathbf{r}_{12}\cdot(\nabla_1-\nabla_2)}{r_{12}}\psi_q(1)\psi_s(2)\, d\tau_1\, d\tau_2\\ &\equiv (pq|\frac{1}{r_{12}}(\mathbf{r}_{12}\cdot(\nabla_1-\nabla_2))|rs).\end{aligned} \tag{14}$$

The latter is an alternative notation which we shall also use for this integral. KK derived such integrals for *s* gaussians, and then used gaussian lobes to represent higher angular momentum gaussians.

In Sect. 2 we describe how we have evaluated (13) and (14) for *s*, *p*, *d* and *f* gaussians using Rys quadrature. In Sect. 3 we present our results for Ne, HF and H_2O and give our assessment of this exciting idea in Sect. 4.

2. Evaluation of the integrals

The evaluation of integrals dominates the time required for SCF and MP2 calculations, so efficient algorithms for integral evaluation are crucial to the success of both procedures. The new KK theory requires integrals not in common use, and algorithms for their evaluation are presented following a summary of the background theory.

The standard electron-electron integrals are

$$(pq|\frac{1}{r_{12}}|rs) = \int \psi_P(1)\psi_Q(1)\frac{1}{r_{12}}\psi_R(2)\psi_S(2)\, d\tau_1\, d\tau_2 \tag{15}$$

where ψ_P, ψ_Q, ψ_R and ψ_S are cartesian gaussians,

$$\psi_P(\mathbf{r}) = X_P^{n_{P_x}} Y_P^{n_{P_y}} Z_P^{n_{P_z}} e^{-\alpha_P(\mathbf{r}-\mathbf{P})^2}. \tag{16}$$

X_P, Y_P and Z_P are components of the vector $(\mathbf{r} - \mathbf{P})$ and $n_P = n_{P_x} + n_{P_y} + n_{P_z}$ is the total angular momentum quantum number.

We have chosen to use the method of Rys, Dupuis and King [13] for the evaluation of the $1/r_{12}$ integrals. The gaussian transform

$$\frac{1}{r_{12}} = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-(ur_{12})^2}\, du \tag{17}$$

is substituted into (15), yielding

$$(pq|\frac{1}{r_{12}}|rs) = \int I_X(u) I_Y(u) I_Z(u)\, du \tag{18}$$

where

$$\begin{aligned} I_X(u) = &\int\int (X_1 - P_x)^{n_{P_x}} \exp[-\alpha_P(X_1 - P_x)^2](X_1 - Q_x)^{n_{Q_x}} \exp[-\alpha_Q(X_1 - Q_x)^2] \\ &\times (X_2 - R_x)^{n_{R_x}} \exp[-\alpha_R(X_2 - R_x)^2](X_2 - S_x)^{n_{S_x}} \exp[-\alpha_S(X_2 - S_x)^2] \\ &\times \exp[-(uX_{12})^2]\, dX_1\, dX_2 \\ \equiv\; & I_X(n_P, n_Q, n_R, n_S, u). \end{aligned} \tag{19}$$

The subsidiary functions $I_X(u)$, $I_Y(u)$ and $I_Z(u)$ are evaluated for particular values of u using recursion relations. The integral is then evaluated exactly by an N-point quadrature formula based on roots and weights from Rys polynomials

$$(pq|\frac{1}{r_{12}}|rs) = \sum_{\alpha=1}^{N} I_X(u_\alpha) I_Y(u_\alpha) I_Z(u_\alpha) w_\alpha. \tag{20}$$

The new integrals (13) and (14) are essentially linear combinations of the $1/r_{12}$ integrals.

The r_{12} integral separates naturally into a sum of three modified $1/r_{12}$ integrals, each containing X_{12}^2, Y_{12}^2 or Z_{12}^2

$$(pq|r_{12}|rs) = (pq|\frac{X_{12}^2}{r_{12}}|rs) + (pq|\frac{Y_{12}^2}{r_{12}}|rs) + (pq|\frac{Z_{12}^2}{r_{12}}|rs) \tag{21}$$

$$= \int I_{Xr_{12}}(u) I_Y(u) I_Z(u) + I_X(u) I_{Yr_{12}}(u) I_Z(u) + I_X(u) I_Y(u) I_{Zr_{12}}(u)\, du \tag{22}$$

where

$$\begin{aligned} I_{Xr_{12}}(u) = &\int\int (X_1 - P_x)^{n_{P_x}} \exp[-\alpha_P(X_1 - P_x)^2](X_1 - Q_x)^{n_{Q_x}} \exp[-\alpha_Q(X_1 - Q_x)^2] \\ &\times (X_2 - R_x)^{n_{R_x}} \exp[-\alpha_R(X_2 - R_x)^2](X_2 - S_x)^{n_{S_x}} \\ &\times \exp[-\alpha_S(X_2 - S_x)^2] \exp[-(uX_{12})^2] \times X_{12}^2\, dX_1\, dX_2. \end{aligned} \tag{23}$$

The modified subsidiary function $I_{Xr_{12}}$ can be evaluated easily. Writing

$$\begin{aligned} X_{12}^2 &= (X_1 - P_x + R_x - X_2 + P_x - R_x)^2 \\ &= X_{1P}^2 + X_{2R}^2 + X_{PR}^2 + 2(X_{1P}X_{PR} - X_{1P}X_{2R} - X_{2R}X_{PR}) \end{aligned} \tag{24}$$

and substituting this into (23) yields

$$\begin{aligned}I_{Xr_{12}}(n_P, n_Q, n_R, n_S, u) &= I_X(n_P+2, n_Q, n_R, n_S, u) + I_X(n_P, n_Q, n_R+2, n_S, u)\\ &+ X_{PR}^2 \times I_X(n_P, n_Q, n_R, n_S, u) + 2[X_{PR} \times I_X(n_P+1, n_Q, n_R, n_S, u)\\ &- X_{PR} \times I_X(n_P, n_Q, n_R+1, n_S, u) - I_X(n_P+1, n_Q, n_R+1, n_S, u)]. \qquad (25)\end{aligned}$$

Thus in order to calculate the r_{12} integrals one first forms modified subsidiary functions $I_{Xr_{12}}$, $I_{Yr_{12}}$ and $I_{Zr_{12}}$ from the conventional subsidiary functions I_X, I_Y and I_Z using (25). The r_{12} primitive integrals are then evaluated using (22).

It is also possible to form the r_{12} integrals in the contracted atomic orbital basis directly without first forming primitive integrals, and the recursion techniques suggested by Obara and Saika [34], and Head-Gordon and Pople [35] are ideally suited to this. Although it is less efficient, we have retained the Rys scheme in this work as it is more easily adapted to produce the $1/r_{12}$, r_{12} and $1/r_{12}(\mathbf{r}_{12} \cdot (\nabla_1 - \nabla_2))$ integrals simultaneously.

The integral $\langle pr|\hat{O}|qs\rangle$, where

$$\hat{O} = \frac{1}{r_{12}}(\mathbf{r}_{12} \cdot (\nabla_1 - \nabla_2)) \qquad (26)$$

separates into three components just like the r_{12} integral. Writing the operator $\hat{O}$ as the sum of its X, Y and Z components

$$\hat{O} = \frac{1}{r_{12}}[X_{12}(\partial/\partial X_1 - \partial/\partial X_2) + Y_{12}(\partial/\partial Y_1 - \partial/\partial Y_2) + Z_{12}(\partial/\partial Z_1 - \partial/\partial Z_2)] \qquad (27)$$

yields

$$\langle pr|\hat{O}|qs\rangle = \int I_{X\nabla}I_YI_Z + I_XI_{Y\nabla}I_Z + I_XI_YI_{Z\nabla}\, du \qquad (28)$$

where

$$\begin{aligned}I_{X\nabla}(n_P, n_Q, n_R, n_S, u) &= -2 \times I_X(n_P, n_Q, n_R, n_S, u)\\ &- \left[\frac{\partial}{\partial Q_x} I_X(n_P, n_Q+1, n_R, n_S, u) + \frac{\partial}{\partial S_x} I_X(n_P, n_Q, n_R, n_S+1, u)\right]\\ &+ \left[\frac{\partial}{\partial S_x} I_X(n_P, n_Q+1, n_R, n_S, u) + \frac{\partial}{\partial Q_x} I_X(n_P, n_Q, n_R, n_S+1, u)\right]\\ &- X_{QS}\left[\frac{\partial}{\partial Q_x} I_X(n_P, n_Q, n_R, n_S, u) - \frac{\partial}{\partial S_x} I_X(n_P, n_Q, n_R, n_S, u)\right] \qquad (29)\end{aligned}$$

and Q_x is the X component of nuclear centre Q. The derivative subsidiary functions such as $(\partial/\partial Q_x)I_X(n_P, n_Q+1, n_R, n_S, u)$ are required in *ab initio* algebraic derivative theory [14], and therefore are readily available in most *ab initio* integral packages.

Each r_{12} and $1/r_{12}$ integral is permutationally equivalent to seven other such integrals. However, the integral $\langle pr|\hat{O}|qs\rangle$ is only equivalent to $\langle rp|\hat{O}|sq\rangle$, although it is related to $\langle qs|\hat{O}|pr\rangle$ by a $1/r_{12}$ integral. Each time an r_{12} subsidiary function or integral $(pq|r_{12}|rs)$ is formed, two non-equivalent $\hat{O}$ subsidiary functions or integrals must be formed. The advantage of producing both the $1/r_{12}$, r_{12} and $\hat{O}$ integrals from modified $1/r_{12}$ subsidiary functions is that all three sets of integrals may be produced simultaneously from an enlarged set of subsidiary functions, with a minimum of redundant calculations and duplicated computer code. The number of unique integrals required for the KK method is $N(N+1)(N^2+N+2)/2$, where N is the number of basis functions.

A standard four index transformation algorithm [36] is used to transform both the $1/r_{12}$ and r_{12} integral from the atomic orbital basis to the molecular orbital basis,

$$(pq|\hat{O}|rs) \rightarrow (IJ|\hat{O}|KL) \tag{30}$$

where $\hat{O}$ is $1/r_{12}$ or r_{12}. However, some minor modifications were required for transformation of the $1/r_{12}(\boldsymbol{r}_{12}\cdot(\nabla_1-\nabla_2))$ integrals because they have lower permutational symmetry. In particular, the standard algorithm produces batches of integrals $(IJ|\hat{O}|KL)$ for fixed J and $I \geqslant J$, $K \geqslant J$, and $L \geqslant J$, where $\hat{O}$ is any of the operators $1/r_{12}$, r_{12} or $1/r_{12}(\boldsymbol{r}_{12}\cdot(\nabla_1-\nabla_2))$. However, since $(IJ|1/r_{12}(\boldsymbol{r}_{12}\cdot(\nabla_1-\nabla_2))|KL) \neq (JI|1/r_{12}\cdot(\boldsymbol{r}_{12}(\nabla_1-\nabla_2))|KL)$, the batch of integrals $(JI|1/r_{12}(\boldsymbol{r}_{12}\cdot(\nabla_1-\nabla_2))|KL)$ must also be produced.

Not all N^4 molecular orbital integrals are required. If there are n occupied molecular orbitals and N molecular orbitals in total, then the required block of molecular orbital integrals is

$$(1\rightarrow N, 1\rightarrow n|\hat{O}|1\rightarrow N, 1\rightarrow n)$$

where $\hat{O}$ refers to any of the operators $1/r_{12}$, r_{12} or $1/r_{12}(\boldsymbol{r}_{12}\cdot(\nabla_1-\nabla_2))$.

Successive batches of molecular orbital integrals are formed, one batch for each operator. Their contribution to the MP2 pair energy and the KK correction term is evaluated and then the integrals are discarded prior to the formation of three more batches. The storage requirement of the four index transformation is N^3. The time taken for the four index transformation is small compared to the time required for evaluation of the atomic orbital integrals.

3. Results

The primitive *sp* sets and contractions used throughout this work are collected in Table 1. The polarisation functions (Table 2) are taken from the work of Pople [21], and larger sets obtained by replacing an exponent α with $(1/2\alpha, 2\alpha)$, $(1/4\alpha, \alpha, 4\alpha)$ and so on.

3.1. Basis set limit MP2-R12 calculations for Ne

In our Ne calculations, we have attempted both to approach the *sp*, *spd* and *spdf* limits for MP2 and MP2-R12 methods as closely as possible, and to devise smaller basis sets which yield acceptable results. We have established four criteria for examining this convergence:

(i) the decreasing SCF energy,
(ii) the decreasing MP2 correlation energy,
(iii) the decreasing value of the completeness relation measured by $|\sum V_{ij}|$, Eq. (9),
(iv) the decreasing value of the completeness relation measured by $|\sum U_{ij}|$, Eq. (10).

Table 1. Primitive and contracted *sp* sets used in this work

Primitive set	Contraction	Reference
9*s*5*p*		15
5*s*5*p*	[51111]*s*5*p*	
4*s*2*p*	[6111]*s*[41]*p*	16
10*s*6*p*		15
6*s*6*p*	[4111111]*s*6*p*	
5*s*4*p*	[62111]*s*[3111]*p*	17
13*s*8*p*		18
8*s*8*p*	[5211111]*s*8*p*	
8*p*6*p*	[5211111]*s*[311111]*p*	
14*s*10*p*		19
7*s*6*p*	$(1\text{–}5)_{1s}(6\text{–}10)_{1s}(6\text{–}10)_{2s}(11)(12)(13)(14)s$ $(6\text{–}10)_{2p}(11)(12)(13)(14)(15)p$	20

Table 2. Polarisation exponents (taken from [21])

Type	H		
p	0.75		
d	1.0		
Type	O	F	Ne
d	1.30	1.65	2.31
f	1.40	1.80	2.70

Table 3 shows how the criteria are affected by the quality of the *sp* basis set used. If we regard the 14*s*10*p* set as the *sp* limit, then only the 8*s*6*p*, 8*s*8*p*, 13*s*8*p* and 7*s*6*p* sets are adequate as far as the SCF energy is concerned. As for the MP2 energy, only the 8*s*8*p* and 13*s*8*p* sets are adequate. However, all basis sets except 4*s*2*p*, 5*s*4*p* and 7*s*6*p* give MP2-R12 values within 0.001 E_h of the 14*s*10*p* value.

Table 4 shows the effect of adding *d* and *f* polarisation functions. It appears that the *spd* limit may have been reached with 5*d* functions. Addition of *d* functions with exponent $\alpha \sim 100.0$ and $\alpha \sim 0.10$ made no difference to the MP2-R12 energy. We note that $|\sum U_{ij}| < |\sum V_{ij}|$ when three *d* functions are present, and understand this by saying that the increments in $|\sum V_{ij}|$ go as

Table 3. Ne calculations using *sp* basis sets. All energies in hartrees

Basis set	$-E_{\text{SCF}} + 128$[a]	$-E_{\text{MP2}}$	$-E_{\text{MP2-R12}}$	$-\sum V_{ij}$	$\sum U_{ij}$
4*s*2*p*	0.492019	0.108132	0.759113	1.80	4.19
5*s*5*p*	0.527247	0.183634	0.651907	1.25	3.24
9*s*5*p*	0.528222	0.184500	0.652220	1.25	3.23
5*s*4*p*	0.535132	0.166148	0.646629	1.30	3.51
6*s*6*p*	0.538079	0.188803	0.652351	1.24	3.22
10*s*6*p*	0.540943	0.189327	0.652566	1.24	3.21
8*s*6*p*	0.546473	0.183692	0.651743	1.25	3.24
8*s*8*p*	0.546473	0.191195	0.652658	1.23	3.20
13*s*8*p*	0.546573	0.191410	0.652765	1.23	3.20
7*s*6*p*	0.546902	0.176957	0.649679	1.26	3.31
14*s*10*p*	0.546902	0.191808	0.652936	1.23	3.20

[a] The Hartree–Fock value is −128.54710 (from [22])

Table 4. Ne calculations at *sp*, *spd* and *spdf* limits. All energies in hartrees

Basis set	$-E_{\mathrm{SCF}}+128$	$-E_{\mathrm{MP2}}$	$-E_{\mathrm{MP2\text{-}R12}}$	$-\sum V_{ij}$	$\sum U_{ij}$
14*s*10*p*	0.546902	0.191808	0.652936	1.23	3.20
14*s*10*p*1*d*	0.546905	0.273167	0.392179	0.31	0.85
14*s*10*p*2*d*	0.546911	0.304489	0.380978	0.17	0.33
14*s*10*p*3*d*	0.546914	0.311960	0.402028	0.14	0.11
14*s*10*p*4*d*	0.546913	0.314546	0.406168	0.13	0.09
14*s*10*p*5*d*	0.546928	0.317628	0.407020	0.13	0.09
14*s*10*p*5*d*1*f*	0.546929	0.342148	0.388865	0.06	0.03
14*s*10*p*5*d*2*f*	0.546930	0.349694	0.387615	0.05	0.02
14*s*10*p*5*d*3*f*	0.546944	0.352298	0.388283	0.04	0.02
16*s*10*p*7*d*3*f*[a]	0.54696	0.35075	0.38855		
valence only					
14*s*10*p*		0.146228	0.591502	1.12	2.24
14*s*10*p*5*d*		0.256964	0.339708	0.11	0.07
14*s*10*p*5*d*3*f*		0.290520	0.320592	0.04	0.01

[a] Kutzelnigg and Klopper, taken from [9]

$(l+1/2)^{-4}$, whilst the increments in $|\sum U_{ij}|$ go as $(l+1/2)^{-6}$, as described by KK. The *spdf* limit appears to have been reached with the 14*s*10*p*5*d*3*f* basis. We note the importance of polarisation functions with small exponents. The addition of a *d* function with $\alpha = 0.2$ lowered the MP2-R12 energy by 0.004 E_h with respect to the calculation carried out with just the tightest 4 functions of the 5*d* set described above.

Table 5 shows results obtained by starting with two smaller basis sets. We find that the 8*s*8*p* results are very close to those obtained with 14*s*10*p*. Indeed, the 8*s*8*p*3*d*1*f* result appears to be nearly as good as the 14*s*10*p*3*d*1*f*, as measured by $\sum V_{ij}$, $\sum U_{ij}$ and the MP2-R12 values. The 6*s*6*p* set appears to give results which are consistently an order of magnitude less reliable.

Using our values for *sp*, *spd* and *spdf* limits, we can estimate the exact MP2 and MP2-R12 values. From the sequence of MP2 values $-0.192\ E_h$, $-0.318\ E_h$, $-0.352\ E_h$, and using the $(l+1/2)^{-4}$ increments we estimate the *spdfg* limit to be

Table 5. Ne calculations using contracted basis sets. All energies in hartrees

Basis set	$-E_{\mathrm{SCF}}+128$	$-E_{\mathrm{MP2}}$	$-E_{\mathrm{MP2\text{-}R12}}$	$-\sum V_{ij}$	$\sum U_{ij}$
6*s*6*p*	0.538079	0.188803	0.652351	1.24	3.22
6*s*6*p*1*d*	0.538091	0.270357	0.390972	0.32	0.86
6*s*6*p*2*d*	0.538592	0.301604	0.379486	0.17	0.34
6*s*6*p*3*d*	0.539049	0.309341	0.401033	0.14	0.12
6*s*6*p*3*d*1*f*	0.539055	0.334260	0.382559	0.07	0.07
8*s*8*p*3*d*1*f*	0.546524	0.335985	0.383394	0.07	0.06
14*s*10*p*3*d*1*f*	0.546914	0.336437	0.383594	0.07	0.06
8*s*8*p*	0.546473	0.191195	0.652658	1.23	3.20
8*s*8*p*5*d*	0.546563	0.317134	0.406788	0.13	0.09
8*s*8*p*5*d*3*f*	0.546566	0.351978	0.388132	0.05	0.02

$-0.364\ E_h$, and using the $1/3(l+1)^{-3}$ as the total error after the l-shell, the full MP2 limit is estimated to be $-0.378\ E_h$. However, using the MP2-R12 values of $-0.653\ E_h$, $-0.407\ E_h$ and $-0.388\ E_h$ with the $(l+1/2)^{-6}$ increments and the subsequent $1/5(l+1)^{-5}$ error, we estimate the MP2-R12 *spdfg* limit to be $-0.384\ E_h$, and the full limit as $-0.382\ E_h$. There is sufficient evidence in the literature to suggest that this is a little above the exact MP2 limit value. Jankowski and Malinowski [23] estimate $-0.387\ E_h$, whilst Petersson et al. [24, 25], using an analytical limiting procedure based on l-convergence suggest $-0.385\ E_h$. Wenzel et al. [32] suggest $-0.385\ E_h$, and Lindgren and Salomonson [33] suggest $-0.388\ E_h$. KK themselves [9] obtain $-0.389\ E_h$ with their *16s10p7d3f* basis, and $-0.388\ E_h$ with a *13s11p10d10f9g5h* STO basis set [8]. The situation will be cleared up when the MP2-R12 *spdfg* results are available. Our calculations suggest that the *g* contribution of $-0.004\ E_h$ is too large to estimate as we have done, and so we must await such calculations.

We may also discuss the valence shell MP2 values, which are $-0.146\ E_h$, $-0.257\ E_h$ and $-0.290\ E_h$, giving an estimated *spdfg* MP2 value of $-0.303\ E_h$. The MP2-R12 values are $-0.592\ E_h$, $-0.340\ E_h$, $-0.321\ E_h$, giving an estimated *spdfg* MP2-R12 value of $-0.317\ E_h$ and a valence MP2-R12 limit of $-0.315\ E_h$. Again, this value is in accord with the most recent best estimates. Taylor [26] argues that his results, using a *[6s6p5d4f3g2h1i]* contracted basis for MP2 ($-0.3118\ E_h$) and CCSD + T ($-0.3164\ E_h$) suggest that the higher order contribution to the Ne valence shell correlation energy is 0.004–0.005 E_h. Sasaki and Yoshimine [27] estimate that the Ne valence shell correlation energy is $-0.321\ E_h$, and thus Taylor [28] believes that the MP2 valence shell energy should be 0.316–0.317 E_h.

3.2. *MP2-R12 calculations for* HF *and* H_2O

Our Ne calculations suggested that the *8s8p* set was a good starting point for reliable MP2-R12 calculations. In Tables 6 and 7, calculations on HF and H_2O

Table 6. HF calculations. All energies in hartrees
$R_e = 1.733\ a_0$

Basis set	$-E_{\mathrm{SCF}}+100$[a]	$-E_{\mathrm{MP2}}$	$-E_{\mathrm{MP2-R12}}$	$-\sum V_{ij}$	$\sum U_{ij}$
[4s2p/2s]	0.021971	0.134235	0.649121	1.54	4.14
[4s2p1d/2s1p]	0.047537	0.212960	0.415723	0.71	2.42
[6s6p/3s]	0.036499	0.197603	0.609361	1.14	3.05
[6s6p1d/3s1p]	0.060569	0.279259	0.384322	0.27	0.66
[6s6p2d/3s2p]	0.063473	0.306216	0.381276	0.15	0.25
[6s6p3d/3s3p]	0.063855	0.312553	0.394175	0.13	0.11
[6s6p3d1f/3s3p1d]	0.065297	0.336270	0.379843	0.07	0.06
[8s8p/7s]	0.043014	0.200838	0.607925	1.13	3.03
[8s8p4d/7s4p]	0.068828	0.318173	0.398777	0.12	0.09
[8s8p4d2f/7s4p2d]	0.070287	0.347984	0.384300	0.05	0.02
15s10p5d2f/10s3p1d[b]		0.34603	0.38459		

[a] Hartree–Fock value is −100.07082 (from [29])

[b] Kutzelnigg and Klopper, taken from [9] ($R_e = 1.7328a_0$)

Table 7. H_2O calculations. All energies in hartrees
$R_e = 1.8088 a_0$, $\alpha = 104.5°$

Basis set	$-E_{SCF} + 76$[a]	$-E_{MP2}$	$-E_{MP2\text{-}R12}$	$-\sum V_{ij}$	$\sum U_{ij}$
[4*s*2*p*/2*s*]	0.009286	0.137846	0.563188	1.34	4.01
[4*s*2*p*1*d*/2*s*1*p*]	0.046405	0.216932	0.364437	0.54	2.21
[6*s*6*p*/3*s*]	0.020219	0.190762	0.549913	1.03	2.80
[6*s*6*p*1*d*/3*s*1*p*]	0.056439	0.272276	0.359328	0.22	0.52
[6*s*6*p*2*d*/3*s*2*p*]	0.060518	0.293961	0.360358	0.13	0.19
[6*s*6*p*3*d*/3*s*3*p*]	0.061264	0.298899	0.367640	0.11	0.11
[6*s*6*p*3*d*1*f*/3*s*3*p*1*d*]	0.062970	0.321045	0.357141	0.06	0.06
[8*s*8*p*/7*s*]	0.025909	0.94459	0.547680	1.01	2.77
[8*s*8*p*4*d*/7*s*4*p*]	0.065199	0.305046	0.372113	0.10	0.08
[8*s*8*p*4*d*1*f*/7*s*4*p*1*d*]	0.066688	0.325728	0.362508	0.05	0.03
[8*s*8*p*4*d*2*f*/7*s*4*p*1*d*]	0.066763	0.330455	0.361889	0.04	0.02
[9*s*7*p*4*d*2*f*/7*s*3*p*1*d*][b]	0.06579	0.33042	0.36049		

[a] Estimated Hartree–Fock limit −76.0675 (from [30]), at $R_e = 1.8111 a_0$, $\alpha = 104.45°$ (experimental values)

[b] Kutzelnigg and Klopper, taken from [9]

are presented, using this and other basis sets described above. As with Ne, we find that *sp* and *spd* limit calculations give MP2-R12 energies below the estimated MP2 limits of $-0.380\ E_h$ for HF and $-0.360\ E_h$ for H_2O [9]. It appears as though *f* functions are still required for reliable molecular calculations with this method.

As a test of the quality of the MP2-R12 wavefunction for HF, we have computed harmonic frequencies using three basis sets from Table 6. These were derived from fits carried out on a 0.001 au grid. Using this procedure, the MP2 frequencies were within 1 cm^{-1} of those obtained using analytic MP2 second derivatives in each case. The HF molecule is well described by MP2, and thus we expected to approach the experimental result closely.

Table 8 shows that for HF there is no significant improvement in accuracy on going from MP2 to MP2-R12. Further investigations are underway to see whether this applies to other molecules.

Table 8. Harmonic frequencies and bond lengths for HF

Basis set	MP2		MP2-R12	
	ω_e/cm^{-1}	R_e/a_0	ω_e/cm^{-1}	R_e/a_0
[4*s*2*p*1*d*/2*s*1*p*]	4211	1.734(9)	4026	1.743(4)
[6*s*6*p*2*d*/3*s*2*p*]	4155	1.732(3)	4157	1.731(6)
[8*s*8*p*4*d*2*f*/7*s*4*p*2*d*]	4146	1.733(0)	4141	1.734(2)
Experimental[a]	4139	1.733		

[a] Taken from [31]

4. Conclusion

In this paper, we have investigated the MP2-R12 method recently suggested by Kutzelnigg and Klopper. Based on our calculations on Ne, NF and H_2O, we find that their simplest scheme is capable of providing near basis set limit MP2 energies if calculations are performed with basis sets of quality $8s8p4d2f$ for first row atoms (~70 basis functions per atom). Four times as many integrals are required, compared with the conventional MP2 method. We believe that this is very significant, because for the first time basis set limit studies are possible for correlated methods. This is because the KK method is able to represent the wavefunction correctly near the electron-electron cusp.

We have started to study molecular properties with this method. Our initial studies on the harmonic frequency of HF appear to suggest that it is not so dependent upon the cusp behaviour as the correlation energy itself.

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